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1979-1980

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1972

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Characterization, and Properties of a New Polymer.
Contract - Research - 1972-1973

A Thermodynamic Study of the Reaction of
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Study of the Reaction of Iron with Carbon
Monoxide and the Effect of Temperature
on the Rate of Reaction

Thermodynamic Properties of the Reaction of
Iron with Carbon Monoxide

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Part 1: STRUCTURAL, SPECTRAL, AND MAGNETIC PROPERTIES
OF A COPPER(II) BIMETALLOMER

Part 2: THERMODYNAMIC, ESR, AND HYDROGEN BONDING STUDIES
OF COBALT DIOXYGEN COMPLEXES

Kenneth A. Leslie

Final Seminar

July 10, 1979

Part 1

An earlier X-ray crystallographic investigation [1] indicated that the complexes $\text{Cu}(\text{salen})$ and $\text{Co}(\text{hfac})_2$ reacted to form the bimetallomer $\text{Cu}(\text{salen})\text{Co}(\text{hfac})_2$ in which the oxygen donor atom of salen was simultaneously coordinated to copper and cobalt. In the course of characterizing this compound and others of the form $\text{M}(\text{salen})\text{M}'(\text{hfac})_2$ [2], it was found that they had good solubility in CH_2Cl_2 , unlike many other binuclear complexes. Thus, a variety of physical methods could be used to study the effect that one metal center has on the chemistry of the second metal center.

The bimetallomer $\text{Cu}(\text{salen})\text{Cu}(\text{hfac})_2$ was prepared and since it contains two different copper(II) environments (six-coordinate and four-coordinate), magnetic susceptibility and ESR spectral studies were undertaken in order to characterize the system. Variable temperature magnetic susceptibility measurements indicate an antiferromagnetic exchange interaction with a coupling constant, J , between the copper(II) centers of -20.4 cm^{-1} . This value of J was relatively small compared to other symmetric copper(II) bimetallomers and different from the value expected from theory [3,4] for a symmetric bimetallomer (with a bridge angle corresponding to that found in the copper-cobalt adduct).

In order to explain these results, a single crystal X-ray diffraction study was carried out. The compound crystallizes in the triclinic space group $\text{P}\bar{1}$ with four molecules in the unit cell. The reduced cell parameters are $a = 17.03(4) \text{ \AA}$, $b = 19.11(4) \text{ \AA}$, $c = 9.89(2) \text{ \AA}$, $\alpha = 96.58(11)^\circ$, $\beta = 100.10(16)^\circ$, $\gamma = 107.70(13)^\circ$. The structure was refined by full-matrix least-squares methods to a weighted R factor of 0.074 for data with $F_o \geq 3\sigma_F$. The structural results indicate that the reduced value of J is due to the low symmetry of the bridge area which allows for only one phenolic oxygen to participate in the superexchange pathway [5]. The investigation of a related system appears to give similar results [6].

Part 2

There has been a great amount of work in the literature dealing with the ability of many tetradentate and pentadentate cobalt(II) complexes to reversibly bind dioxygen [7,8]. Much of this research was in part due to a desire to understand the factors involved in the binding of dioxygen in biological systems.

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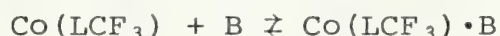
Part 2

There has been a great amount of work in the literature dealing with the ability of many tetradentate and pentadentate cobalt(II) complexes to reversibly bind dioxygen [7,8]. Much of this research was in part due to a desire to understand the factors involved in the binding of dioxygen in biological systems.

The cobalt dioxygen adducts were considered as models since they have one unpaired electron, allowing their electronic structure to be probed using ESR spectroscopy. In addition, potential industrial applications were recognized leading to the use of cobalt(II) complexes as catalysts for selective and controlled oxidations of organic substrates, most notably phenols [9].

Previous studies have elucidated some of the factors involved in the binding of dioxygen to the porphyrin Co(PPIXDME) [10]. It was felt that the Co(PPIXDME) results would provide a foundation for examining the thermodynamic and electronic properties of cobalt(II) Schiff-base complexes. By investigating these properties, it was hoped that the catalytic activity of the complexes would be better understood. Derivatives of the Schiff-base complex Co(saloph) were synthesized which were more soluble than the parent complex in toluene and CH_2Cl_2 . The ligand system formed by the condensation of 4,6-dimethoxysalicylaldehyde with 4-trifluoromethyl-o-phenylenediamine yielded the most soluble cobalt(II) complex, abbreviated Co(LCF₃).

This complex was shown via ESR studies to form both 1:1 and 2:1 adducts with strong bases. The 1:1 base adduct reversibly forms a dioxygen adduct at low temperature. The fractional amount of an electron transferred from cobalt to oxygen was calculated as a function of axial base, and found to follow the trend predicted by the "spin-pairing model" [11]. The enthalpy for the reaction



was measured for the bases piperidine, 1-methylimidazole, pyridine, and tetrahydrothiophene. A good fit to the E and C equation was obtained for all bases except piperidine, where hydrogen bonding contributes to the enthalpy. The corresponding oxygen enthalpies



were also determined.

An additional probe of the bound dioxygen was undertaken using infrared spectroscopy. Due to the insensitivity of the O-O infrared stretching frequency as a function of ligand environment, 2,2,2-trifluoroethanol, TFE, was added to oxygenated CH_2Cl_2 solutions of the neutral pentacoordinate Schiff-base complex Co(SalMeDPT). The O-H frequency shift was then used to obtain information concerning the nature of the bound dioxygen.

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A THERMODYNAMIC STUDY OF METAL CARBOXYLATES

John R. Long

Final Seminar

September 18, 1979

In recent years, considerable interest has been generated in the area of metal cluster chemistry. Clusters are found in a variety of important biological systems [1,2], and are reported to effect some intriguing, industrially important reactions. Different mechanisms have been suggested to account for the synergistic ways in which one metal can influence the chemistry at a second metal site [3]. A more complete understanding of this area leading to a full appreciation of the potential of metallomers for novel reaction types will require extensive investigation of many different types of systems. In addition to structural investigations, quantitative studies of chemical reactivity (kinetic and thermodynamic) must be carried out to determine ways and extents to which a second, third, etc., metal atom in a molecule can influence the coordination chemistry and redox chemistry at the first metal site.

Dimeric metal carboxylates were chosen for such a study because of the extensive structural information available on them [4,5]. Initially the thermodynamics of adduct formation for 1:1 and 2:1 adducts formed by Lewis bases with $\text{Rh}_2(\text{C}_4\text{H}_7\text{O}_2)_4$ were studied in benzene solutions [6]. Electrochemical studies of these adducts were carried out in methylene chloride solutions. Corrections for a benzene-acid interaction were necessary to obtain solvent minimized enthalpies of acid-base adduct formation. The thermodynamic data clearly demonstrates substantial changes in the acidic and redox properties of the second metal as a result of base coordination to the first. The metal-metal bonding in the system causes this dimer to be a most unusual Lewis acid, as evidenced by deviations of the E and C predicted enthalpies from those observed. The unusual Lewis acid properties are attributed to the enhanced π -backbonding capability of the rhodium(II) center as a result of extensive mixing of orbitals with π -symmetry on the two metal centers. This causes the rhodium(II) center to be very effective in π -backbonding to the ligands. The reduction potentials of $\text{Rh}_2(\text{C}_4\text{H}_7\text{O}_2)^+$, $\text{Rh}_2(\text{C}_4\text{H}_7\text{O}_2)_4\text{B}^+$ and $\text{Rh}_2(\text{C}_4\text{H}_7\text{O}_2)_4\text{B}_2^+$ are analyzed, and provide further support for the extensive π -backbonding capabilities of this metal cluster.

Thermodynamic and spectroscopic studies of rhodium perfluorobutyrate were performed to determine the role of the bridging ligands in the Lewis acid properties of metal carboxylates. The thermodynamic data clearly demonstrates substantial changes in the acidic properties of the second metal as a result of base coordination to the first, as was seen for rhodium butyrate. Again, deviations of the observed enthalpies from those predicted by the E and C equation indicates the π -backbonding capability of rhodium perfluorobutyrate. The main effect of the fluorination of the bridging ligand is to make the rhodium centers better electron pair acceptors.

A proposed molecular orbital diagram [6], predicts that dimeric molybdenum carboxylates are incapable of π -backbonding since they do not possess electron density in the π^* orbital, as do the rhodium carboxylates; for this reason a study of molybdenum perfluorobutyrate was performed. Thermodynamic data for six bases clearly demonstrates substantial changes in the acidic properties of the second metal as a result of base coordination to the first. Deviations of the observed enthalpics from those predicted by the E and C equation were $.3 \text{ kcal}\cdot\text{mol}^{-1}$ or less for all bases studied. As a result, π -backbonding is believed to be insignificantly small or absent in the metal-ligand bonds of molybdenum perfluorobutyrate.

The conclusion can be stated with the following generalization for metal-metal bonded systems: the σ , π , or δ basicity of a transition metal ion in a given oxidation state is maximized if that ion is present as a d^8-d^8 , d^7-d^7 , or d^5-d^5 dimer, in which σ^* , π^* , or δ^* is the highest occupied molecular orbital, respectively. Similarly, the σ , π , or δ acidity is maximized in a d^0-d^0 , d^1-d^1 , or d^3-d^3 dimer, in which σ , π , or δ is the lowest unoccupied molecular orbital, respectively. This conclusion relies on the maintenance of the MO ordering depicted in Figure 3 and a low spin disposition of electrons; an assumption that appears to be valid in the vast majority of neutral homonuclear dimers [7].

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ORGANO Os₃ CLUSTER CHEMISTRY: HYDRIDO-CH₃, -CH₂, -CH,
AND RELATED COMPOUNDS

R. B. Calvert

Final Seminar

September 20, 1979

Interest in transition metal cluster chemistry has increased sharply over the past decade as evidenced by the dramatic rise in the number of reported molecular transition metal clusters. The development of cluster chemistry has been facilitated by technological advances in physical characterization techniques. Current interest is a result, in part, of the proposition that discrete molecular clusters may be reasonable models of metal surfaces with respect to the processes of chemisorption and catalysis [1].

Hydrido-hydrocarbyl [2] species have been proposed as important intermediates in a wide variety of reactions ranging from stoichiometric mononuclear chemistry to catalytic industrial processes. Despite the importance of this class of compounds few examples are known [3]; polynuclear systems are even more rare. Shapley and Keister proposed the intermediacy of a polynuclear hydrido-ethyl compound, $\text{HOs}_3(\text{CO})_{10}\text{CH}_2\text{CH}_3$, during the course of the reaction of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and ethylene [4]. Attempts to prepare isolable hydrido-alkyl clusters led to the synthesis of $\text{HOs}_3(\text{CO})_{10}(\text{CH}_2\text{COOEt})$ by reaction of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with ethyldiazoacetate [5]. The success of this reaction suggested the use of other diazo compounds which lacked potential coordinatry groups.

Reaction of the unsaturated cluster $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with CH_2N_2 results in formation of the yellow compound " $\text{Os}_3(\text{CO})_{10}\text{CH}_4$ " which exists in solution in two isomeric forms, a methyl-hydride cluster, $\text{HOs}_3(\text{CO})_{10}\text{CH}_3$, and a methylene-dihydrido species, $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{CH}_2$ [6]. These isomers have been shown to be tautomers; they are rapidly interconverting in solution above 0°C. An equilibrium isotope effect on hydrogen and deuterium distribution within these compounds has been observed using ¹H NMR and confirmed in the methylene case by neutron diffraction [7]. An equilibrium isotope effect can be shown to be consistent with the equilibrium, $\text{HOs}_3(\text{CO})_{10}\text{CH}_3 \rightleftharpoons \text{H}_2\text{Os}_3(\text{CO})_{10}\text{CH}_2$. Carbon monoxide dissociation from $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{CH}_2$ can be effected by pyrolysis, photolysis, or addition of $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ and results in formation of the methylidyne cluster, $\text{H}_3\text{Os}_3(\text{CO})_9\text{CH}$. Structural proposals feature a triply bridging CH moiety in the methylidyne cluster, a symmetrically bridging methylene ligand [8], and an asymmetrically bridging methyl group in $\text{HOs}_3(\text{CO})_{10}\text{CH}_3$ [9]. A potentially general NMR technique, based on partial isotopic incorporation (²H for ¹H) and variable temperature NMR for determining C...H...M interactions has been presented [9].

$\text{HOs}_3(\text{CO})_{10}\text{CH}_3$ reacts readily with a variety of nucleophiles including CO, H₂, PMe_2Ph , CH_3CN , NCCH_3 , MeOH, ethylene, cyclooctene, and Et_3SiOH [10]. Reductive elimination of methane is observed in each case. No intermediate of the type $\text{HOs}_3(\text{CO})_{10}(\text{L})\text{CH}_3$ has been observed in contrast to the chemistry of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ [11]. We attribute the fact that we have not been able to observe an intermediate of this type to the relative instability of a hydrido-(terminal) methyl compound.

The results of our work with the series of compounds, $\text{HOs}_3(\text{CO})_{10}\text{CH}_3$, $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{CH}_2$, and $\text{HOs}_3(\text{CO})_9\text{CH}$ suggest that α -H transfer is a more facile process than we originally anticipated. In fact, it is reversible and we have observed directly, for the first time, the interconversion of metal-bound alkyl and alkyldiene-hydride fragments. Our work with other cluster-hydrocarbyls suggests that the observation of reversible α -H transfer is a general phenomenon. Thus, CF_3CHN_2 , CH_3CHN_2 , $\text{Me}_3\text{SiCHN}_2$, $\text{N}_2\text{CHCOOMe}$, and $\text{N}_2\text{CHCOOEt}$ have been used to prepare hydrido-hydrocarbyl species by reaction with $\text{H}_2\text{Os}_3(\text{CO})_{10}$. In all cases, the data supports interconverting hydrido-alkyl and dihydrido-alkyldiene species.

Various aspects of the system described here, for a metal triangle, have been proposed for metal surface reactions. The triosmium system presented here may well provide a model for the interaction of a C_1 fragment with a metal surface as in the processes H/D exchange, methanation, and hydrocarbon hydrogenolysis.

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THERMODYNAMIC CHARACTERIZATION OF Ni(tfacDPT)

Robert G. Mayer

Final Seminar

September 24, 1979

Five-coordinate complexes of first-row transition-metal ions may be expected to act as Lewis acids, binding to Lewis bases to form one-to-one adducts. Where such neutral complexes are soluble in weakly-interacting solvents, the solvent-minimized enthalpies of adduct formation may be used as estimates of the energy of the bond formed between the metal ion and the monodentate ligand. Thermodynamic data on a set of systems where only the metal ion or only the pentacoordinating chelate were varied would provide a quantitative basis for analyzing the differences in reactivity of transition-metal complexes. The method of choice for determining enthalpies of adduct formation is calorimetry, as the enthalpy is determined directly. If, for reasons of low enthalpy, a small equilibrium constant, or poor solubility, the calorimetric experiment fails, determination, by NMR or spectrophotometry, of the equilibrium constant at various temperatures may yield the enthalpy via the van'tHoff equation.

In these enthalpic determinations it is important that the stoichiometry of the reaction be known. All the methods for determination of the enthalpy in this research permit confirmation of the expected one-to-one stoichiometry, however, no discrimination can be made between a system which forms only one complex of the expected stoichiometry and one in which the complex is present as several isomers.

In previous work, determination of enthalpies of adduct formation between two complexes, Ni(SDPT) [1] and Ni(SMDPT) [2], was made with a limited set of bases. Both low solubility and low acid strength hindered the thermodynamic characterization of these complexes. The compound Ni(tfacDPT) has neither of these shortcomings and enthalpies of adduct formation have been determined in its reactions with 1-methylimidazole, 4-picoline, 4-picoline-N-oxide, dimethylsulfoxide and hexamethylphosphoramide, all using toluene as the solvent.

Enthalpies and equilibrium constants for adduct formation have been determined for the reaction of 4-picoline with Ni(SDPT), Ni(SMDPT) and Ni(tfacDPT). The enthalpy for the latter compound is the most negative of the three; it also has an anomalously large equilibrium constant. The significance of the enthalpies and the entropies of adduct formation can be analyzed by use of an enthalpy vs. entropy plot [4].

The thermodynamic parameters for the bases 1-methylimidazole, 4-picoline and dimethylsulfoxide were determined calorimetrically. To obtain the best possible determination of the enthalpy by NMR for 4-picoline-N-oxide and hexamethylphosphoramide a new method for analyzing the data has been developed. In the former method one would determine, at a given temperature, both the equilibrium constant K , and the chemical shift difference between the free and complexed base, $\Delta\omega^O$, by obtaining an observed change in chemical

shift, $\Delta\omega_{\text{obs}}$, for each of a number of solutions using the equation:

$$K^{-1} = [B^O] \frac{\Delta\omega_{\text{obs}}}{\Delta\omega^O} + [A^O] \frac{\Delta\omega^O}{\Delta\omega_{\text{obs}}} - ([A^O] + [B^O])$$

From the temperature dependence of K, the enthalpy and the entropy of adduct formation could be determined. It is possible to recast the temperature-dependent terms K and $\Delta\omega^O$ into four temperature-independent terms, including ΔS and ΔH , and fit all the solutions at all the temperatures simultaneously. This method allows more data to be used, takes advantage of the temperature dependence of the chemical shift, and generates valid statistics.

At least one of the bases, hexamethylphosphoramide, has an enthalpy which indicates a significant steric hinderence to complex formation. In spite of this effect the five bases in their reaction with Ni(tfacDPT) give a good enthalpy vs. entropy plot.

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COOPERATIVITY AND SPIN-DYNAMICS IN IRON(III) SCHIFF-BASE COMPLEXES
EXHIBITING SPIN-CROSSOVER PHASE TRANSITIONS

Muin Shawki Haddad

Final Thesis Seminar

November 5, 1979

Interest in the spin-crossover phenomenon, where a metal complex interconverts between two electronic states with differing spins has been growing. Specifically, interest has focused on iron in the +3 (d^5) and +2 (d^6) oxidation states. It has been observed that certain iron-containing proteins undergo a high-spin to low-spin conversion [1-3]. An important goal of the study of spin-crossover systems is gauging the rate at which the spin is flipping and its relation to the electronic structure of the molecular system. This type of understanding is essential to the general area of electron transfer.

The variation of the relative concentration of high-spin and low-spin molecules is expected to follow a Boltzmann distribution determined by the relative magnitude of the thermal energy and the energy separation between the two spin-states. In practice, this situation is not realized for solid samples, but, instead, astonishing results have been noted for the variation of the effective magnetic moment per iron with temperature. The most puzzling observations are the incompleteness of the conversion in the solid state at low temperatures and the suddenness of the conversion in some cases. For those complexes that exhibit an incomplete transition, an intermediate spin-state has been invoked without adequate support [4].

A program was initiated to elucidate the various puzzling phenomena encountered with spin-crossover complexes. A series of ferric compounds that exhibited the various peculiarities were synthesized. The compounds were obtained by the Schiff-base condensation of salicylaldehyde (or derivatives) and N-ethylethylenediamine and the subsequent chelation of iron(III). The compounds studied in this work have the general formula $[\text{Fe}(\text{X-SalEen})_2]\text{Y}$ where X is H, 3-OCH₃ or 5-OCH₃ and Y is NO₃⁻, PF₆⁻ or BPh₄⁻. Variable-temperature magnetic susceptibility, EPR and ⁵⁷Fe Mössbauer data were collected.

It was our hypothesis that the spin-crossover phenomenon is a phase transition occurring via the general "Nucleation and Growth" mechanism for phase transitions [5,6]. The mechanism involves formation of nuclei of the new phase in domains of the old phase and the subsequent growth of the nuclei. Nuclei formation and their growth are cooperative phenomena that are sensitive to the degree of imperfection in the crystal system. Two major perturbations were, consequently, carried out. The first involved grinding the crystalline compounds and the second involved doping the iron compounds into isostructural cobalt(III) and chromium(III) compounds.

A spectacular result was noted. It was found that grinding, and consequently increasing the number of defects, leads to an incompleteness for a transition that is normally complete for the crystalline samples. Moreover, grinding and doping caused the transition to be more gradual compared to the crystalline compound. It was found that several of the effects are very pronounced for the compound $[\text{Fe}(3\text{-OCH}_3\text{SalEen})_2]\text{PF}_6$. This compound undergoes a sharp and complete transition from high-spin to low-spin within few degrees as an unperturbed crystalline compound.

It is speculated that the activation barrier created by grinding could be caused by growth site impingement of the minority-spin domains. It would be expected that the number of nuclei to be more abundant in the ground samples because defects are preferred sites of nucleation. A larger activation barrier could also be the result of the interaction of the moving interface (that exists between the old and new phases) with dislocations in the ground samples or Co(III) and Cr(III) complexes in the doped samples.

Mössbauer and EPR data discount the presence of an intermediate spin-state and establish the existence of two electronic states, the high-spin state (6A_1) and the low-spin state (2T_2).

In conclusion, our findings strongly suggest that spin-crossover occurs by a phase transition where the "Nucleation and Growth" mechanism is operative.

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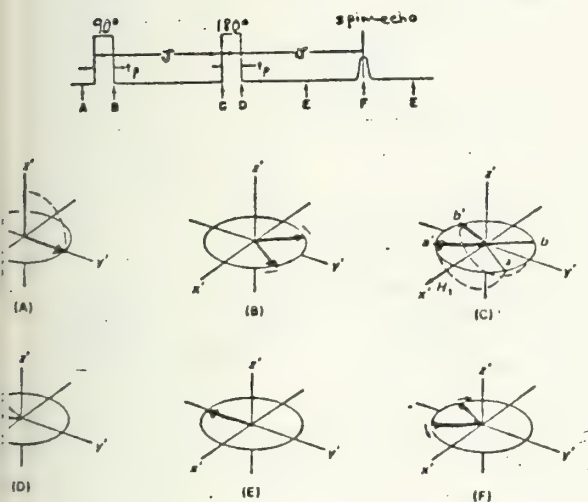
Applications of Fourier Transform EPR to Inorganic Chemistry

Barry B. Corden

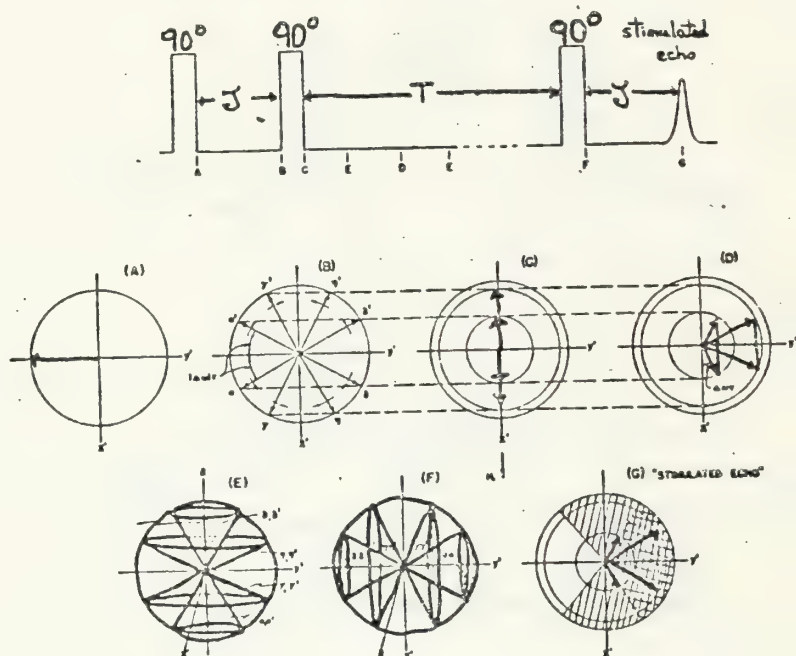
November 13, 1979

Although electron spin-echo spectroscopy is hardly a commonplace experimental method, it has been used to study paramagnetic systems for nearly 30 years. The spin-echo technique was discovered by Hahn [1] for proton resonance in the early 1950's, and later modified to study unpaired electrons [2]. Hahn's spin-echo method, along with another routinely used pulse sequence, is outlined below [3]. The advantage of the stimulated-echo experiment is that it allows one to detect the echo for longer times. The spin-echo experiment is limited by the relatively short phase memory of the spin system, while the stimulated-echo experiment is limited by the spin-lattice relaxation time.

Hahn Spin-Echo (2 pulse sequence)



Stimulated-Echo (3 pulse sequence)



$$\begin{aligned} T &\sim 1 \text{ msec} \\ \tau &\sim 0.1 - 1 \mu\text{sec} \\ \tau_p &\sim 1 \text{ nsec} \end{aligned}$$

Fig. 1

If an r.f. frequency is applied during T , the pulse-ENDOR experiment can be performed.

Inhomogeneous line broadening in amorphous glass or powder samples often restricts definitive conventional EPR studies to

single crystals. Pulse techniques are not hindered by this problem. This is because the pulse width is on the order of only a few gauss. Hence, only a small portion, such as a single hyperfine line, of the entire spectrum is irradiated by the microwave pulse. This point is depicted schematically. Continuous wave EPR spectra are usually displayed in the derivative form (A). Integration of (A) yields the corresponding absorption spectrum (B). Spectrum (B) is an envelope of three poorly resolved absorption lines (C). These three lines can be selectively irradiated by different pulses (D) (e.g. three different pulse experiments).

The superhyperfine structure shows up as modulation of the spin echo envelope [4]. This is extremely important: the amplitude of the spin echo does not steadily decrease with increasing T , it oscillates. From the modulation frequency and depth of the spin echo envelope; the identity, number, and distance of surrounding nuclear spins from the unpaired electron can be determined.

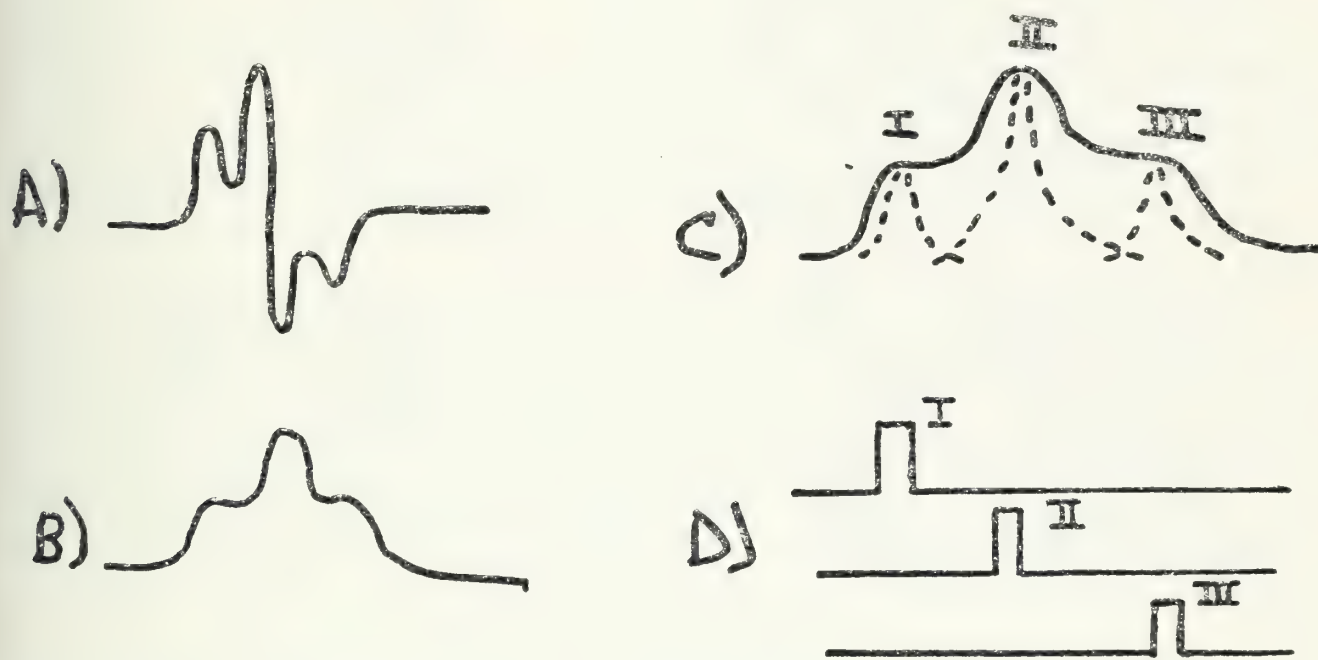


Fig. 2

Additional structural information can be obtained by measuring the Linear Electric Field Effect (LEFE) [5]. Application of an electric field to a paramagnetic sample results in a shift in the resonance lines if the unpaired electron is situated in a non-centrosymmetric ligand field. The magnitude of the shift is proportional to the deviation from inversion symmetry. Due to inhomogeneous line broadening, and the small shifts that are commonly observed by this effect, conventional EPR cannot readily detect the LEFE. Since the pulse technique is not affected by inhomogeneous line broadening, it serves as a very sensitive probe for the LEFE. Thus, pulse spin-echo spectroscopy yields quantitative

structural information about paramagnetic centers in powders or amorphous samples.

Many biological metalloproteins cannot be obtained in well ordered single crystals large enough for conventional EPR studies. Since proteins need not be single crystals for pulse techniques to provide valuable information, considerable attention has been paid to both iron [6] and copper [7] in biological systems. The results for these systems will be discussed extensively during the seminar in order to demonstrate what kinds of problems accompany pulse experiments and Fourier Transforms of the spin-echoes.

Recently, pulse spin-echo EPR has been successful in studying optically induced triplet states [8]. This work was rapidly extended to successfully probe photosynthetic systems [9] (e.g. chlorophyll in vivo as well as model reaction centers in vitro). In this experiment the photolysed reaction center (electron-transfer acceptors have been chemically reduced) exhibits an intense EPR triplet signal. Further examination of this signal indicates that the system is electron spin polarized [10]. This means that a non-Boltzmann distribution of populations of the triplet levels exists due to unequal rates of population and depopulation of the different levels. Kinetic information can help elucidate the true nature of the reaction center in Chlorophyll. Kinetic studies using pulse methods have a time resolution on the nanosecond time scale, while kinetic studies with conventional EPR spectrometers are limited to a microsecond time scale.

In the next several years one can expect to see several developments in pulsed-EPR technology. First, extended studies using Q-band frequencies are just now becoming possible. Significant strides in taking rapid Fourier Transforms of the FID or spin-echo can make this a more routine operation. This has several advantages over a more time consuming simulation of the spin-echo modulation pattern which is a commonly used technique for obtaining quantitative information. Finally, the potential for increased sensitivity of the pulse method has yet to be fully realized.

Future projects might include extensive studies of other paramagnetic ions, quadrupolar interactions of the ligands, mechanisms of electron spin relaxation at low temperatures, and kinetic studies of transient species.

These developments will make FT-EPR an invaluable experimental method to chemists in the future.

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Nitrogen-14 Nuclear Quadrupole Double Resonance Studies of Nitrogenous Bases

William L. McCullen

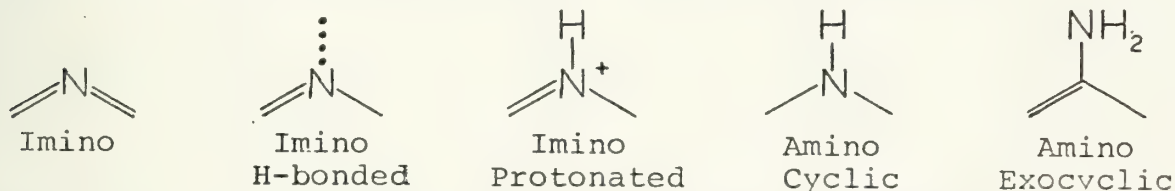
November 19, 1979

The interaction of metal ions with nucleic acids in biological systems is well documented.[1] There is a great deal of evidence which suggests that in many cases metal ions coordinate to nitrogen sites of the pyrimidine and purine bases of the nucleotide unit. Previous work[2,3] has demonstrated that ^{14}N nuclear quadrupole resonance spectroscopy is an excellent means of investigating the interaction of diamagnetic metal ions with nitrogen donor ligands. The application of this technique to the study of metal-nucleic acid interactions is a logical extension of that work. However, the complexity of the pyrimidine and purine bases and the limited reports of ^{14}N NQR results for these compounds preclude the investigation of metal-nucleic acid interactions. The purpose of this work is to apply ^{14}N nuclear quadrupole resonance spectroscopy to the study of these heterocyclic nitrogenous bases and to develop techniques which will allow the unambiguous assignment of the observed resonances.

The detection of ^{14}N nuclear quadrupole resonances using conventional techniques is quite difficult due to the inherent insensitivity of transitions in the range 0.2- 4.0 MHz, and the long ^{14}N spin-lattice relaxation times (>30 seconds) frequently encountered. These problems are avoided in the double resonance via level crossing (DRLC) experiment.[4] In this technique, the sample is placed in a large static magnetic field which results in polarizing the proton spin bath. Next, the protons are adiabatically demagnetized by moving the sample to a region of zero applied field. During this process, there is an exchange of spin energy between the proton and nitrogen spin baths via a resonant interaction known as level crossing which enhances the polarization of the nitrogen quadrupole levels. At zero field, the sample is irradiated at a selected frequency in an attempt to saturate a nuclear quadrupole transition. Following this, the proton spin bath is adiabatically remagnetized by returning the sample to the high field region. As before, the nitrogen and proton spin baths interact via level crossing during this process. Finally, a low resolution nmr spectrometer detects the recovered proton magnetization. The irradiation frequency is incremented and this cycle is repeated until the desired spectral range is swept. The spectrum produced is a plot of the recovered proton magnetization as a function of the irradiation frequency. If the irradiation frequency corresponds to a nuclear quadrupole transition, energy is absorbed by the nitrogen spin bath and subsequently transferred to the proton spin bath during the second level crossing. As a result, the recovered proton magnetization is smaller than would be detected in absence of the excitation of a nuclear quadrupole transition.

Ideally, three transitions (ν_+ , ν_- , and ν_0) are detected for each non-equivalent nitrogen from which the NQR parameters, the quadrupole coupling constant (e^2Qq/h) and the asymmetry parameter (η), are calculated. Generally, however, ν_- transitions are often quite weak or even unobservable. Also, in many instances, several transitions overlap each other and are difficult to resolve. These situations render the determination of the NQR parameters and their assignment to the proper nitrogen site extremely difficult. In an attempt to overcome these difficulties, the DRLC experiment was modified to include two double irradiation techniques: sensitivity enhancement[4] and pre-saturation. The former technique enhances the intensity of the intrinsically weak ν_- transitions which allows the unambiguous coupling of the three transitions associated with a single nitrogen. The pre-saturation technique provides a means of eliminating the "overlapping" resonance from the spectrum.

A number of pyrimidine and purine derivatives were studied using the DRLC-double irradiation techniques. With a few exceptions, most of the nitrogen sites of the compounds considered fall under one of the five categories shown below.



Among all of the compounds studied, it was discovered that the majority of the observed quadrupole coupling constants fall within well-defined ranges quite characteristic of the various nitrogen environments. Of particular interest is the observation that the quadrupole coupling constants of imino nitrogens are quite sensitive to hydrogen bonding. The relative intensities of corresponding transitions among the different types of nitrogen sites is shown to be a function of the proximity of the nearest proton. Those nitrogens directly bonded to protons exhibit quadrupole transitions of much greater intensity than the transitions of those nitrogens not directly bound to protons. Finally, the solid state effect[4], a second order dipolar interaction between the ^{14}N and ^1H nuclei which gives rise to fine structure and multiple quantum transitions, is discussed.

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One Dimensional Magnetic Systems

Warren L. Nehmer

November 20, 1979

Introduction:

Magnetic interactions between transition metals bridged by ligands have been intensely studied for many years. Magnetic interactions occur in dimers, trimers, tetramers, clusters, linear chains, planes, and 3-dimensional arrays. Of particular interest to many solid state physicists and chemists are the magnetic interactions occurring in linear chains [1].

General Considerations:

When referring to extended magnetic interactions there are two types of dimensionality to be distinguished from one another; space dimensionality and spin dimensionality [2]. Space dimensionality refers to the restriction of exchange pathways, hence a one dimensional system can undergo exchange only along one axis. Spin dimensionality is exemplified by the magnetic spin Hamiltonian:

$$H = -\sum (2JS_z^i S_z^j + 2JS_x^i S_x^j + 2JS_y^i S_y^j)$$

with three limiting cases:

- 1) Heisenberg $H = -2J\sum S_i S_j$
- 2) XY $H = -2J\sum (S_x^i S_x^j + S_y^i S_y^j)$
- 3) Ising $H = -2J\sum (S_z^i S_z^j)$

Thus systems with a space dimensionality of one may have spin dimensionalities of one, two, or three. Examples of one dimensional systems that follow Ising [3], XY [4], and Heisenberg [5] magnetic models have been prepared and characterized. As in nature, most of the magnetic interactions of one dimensional systems are anti-ferromagnetic. Recently a very good example of a ferromagnetic spin -1/2 Heisenberg linear chain, (CuCl₂·TMSO), was prepared and characterized [6].

Applications:

Nickel and cobalt hippurate complexes have been shown to exhibit pseudo one-dimensional magnetic interactions [7]. These hippurate systems are of interest since they possess a variety of different magnetic interactions including isotropic superexchange,

anisotropic superexchange (Dzyaloshinsky-Moriya interaction) and interchain dipolar exchange. Thus these systems have been shown to exhibit a metamagnetic transition at low temperature.

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Chemoprevention of Cancer: Anticancer Effects of Selenium and Selenite

Mary M. Fox

November 27, 1979

Cancer accounts for nearly 20% of the deaths of the population in the West [1]. Though intense research and study into the mechanisms of cancer have produced many anticancer drugs, more dramatic measures are needed. Measures which provide new and more potent anticancer agents than are presently available. The trace element selenium was recommended for cancer therapy as early as 1915 [2]. And in 1949, Clayton and Baumann were the first to demonstrate the anticarcinogenic effects of dietary selenium in animal experiments [3]. Though acute toxicity and even carcinogenicity have been linked with selenium, recent studies demonstrate quite significantly the anticarcinogenic effects of selenium. These studies suggest the possibility of supplementing our diet with selenium as a preventive measure against cancer.

The biochemical significance of selenium in animals is that of being an essential component of glutathione peroxidase. Glutathione peroxidase catalyzes the action of reduced glutathione (GSH) in converting peroxides (and hydroperoxides) to H_2O (and the corresponding alcohols) and dioxygen. This enzyme functions to protect cells and biological membranes against oxidative damage. The peroxides formed by oxidases destroys pyrimidine moieties of nucleotides resulting in DNA damage. It is this role as an antioxidant that is believed to be one of the mechanisms whereby selenium inhibits tumor formation [4,5].

It has been suggested that selenium is protective against formation of malonaldehyde, a product of peroxidative tissue damage which is carcinogenic [6]. Dietary experiments in which selenium is administered as sodium selenite to special rat strains show anticarcinogenic effects and also a protective effect against carcinogen-induced chromosome damage. Antioxidants (selenium, d,l- α -tocopherol and ascorbic acid) when applied to mouse skin, reduced skin tumor formation induced by 7,12-dimethylbenz(α)anthracene and croton oil and reduced incidence of hepatic tumors induced by N-2-fluorenylacetamide and diethylaminoazobenzene after incubation with dilute solutions of H_2O_2 [7,8,9].

Griffin et. al. observed inhibitory effects of selenium on the mutagenicity of acetylaminofluorene (AAF) and of N-hydroxyacetylaminofluorene (NOHAAF). Labeled carcinogen studies of AAF and NOHAAF on female rats revealed lowered binding rates of the carcinogens to liver DNA and t-RNA. From the results of this study, the investigators proposed that selenium acts to inhibit the action of the enzymes that metabolize AAF and NOHAAF and/or selenium acts to increase the level of liver enzymes involved in the detoxification of AAF and NOHAAF [10,11].

In-vivo studies have shown the anticancer effects of selenium. However certain trace elements counteract the cancer protecting effects of selenium. Both arsenic and zinc appear as physiological antagonists of selenium. Joint administration of arsenite and selenite increases the incidence of spontaneous mammary adenocarcinoma in female mice.

The antagonistic effect of arsenic is believed to be due to stimulated biliary excretion of selenium [12]. Studies with zinc in the form of $ZnCl_2$ also abolishes the cancer-protecting effects of selenium. The suggested role of zinc is presumably to prevent the physiological uptake of selenium [13].

From available experimental results beneficial effects are noticeable in selenium supplemented diets of research animals. The question arises as to what the level of selenium supplementation should be to provide optimal cancer protection. The many complications to such a question are: the toxicities of the element itself, its complex interrelationships with other trace elements and the influences of other physiological factors [14,15,16].

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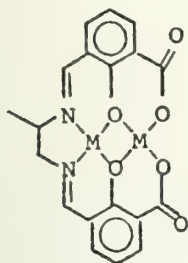
PARAMAGNETIC COMPLEXES OF BINUCLEATING LIGANDS

Russell C. Long

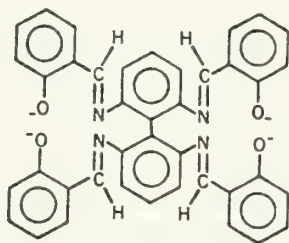
December 4, 1979

Introduction

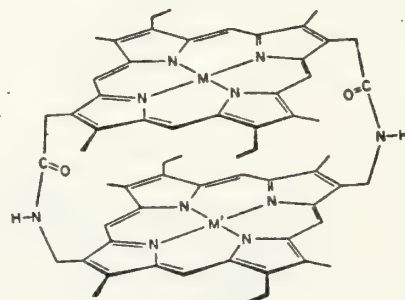
In the last few years, several different types of binucleating ligands and transition-metal complexes of binucleating ligands have been synthesized and studied. Illustrated below are examples of the different types of binucleating ligands:



(a)



(b)



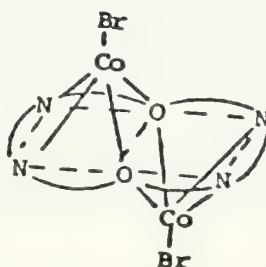
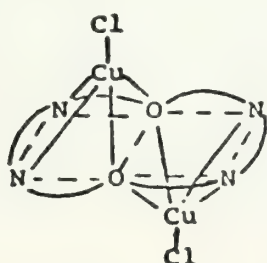
(c)

It is to be noted that the type (a) ligand has a single atom bridging between the two metal ions, whereas the type (b) ligand has a multi-atom bridge. The type (c) ligand is an example of a bisporphyrin. Binucleating ligands can be defined as those ligands which simultaneously bind two metal ions in at least three positions each [1]. This seminar primarily focuses on metal-metal interactions found in complexes of binucleating ligands.

Magnetic Exchange Interactions

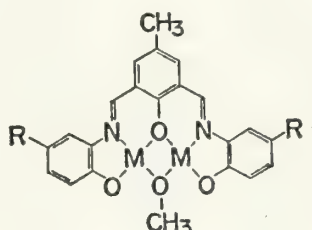
Magnetic susceptibility measurements are a common method used to determine the magnitude and sign of magnetic exchange interactions [2]. Plots of magnetic susceptibility vs. temperature are generally fitted theoretically to Van Vleck's susceptibility equation. From this fitting, the value and sign of J , the magnetic exchange parameter, can be obtained. A positive J value indicates a ferromagnetic interaction and a negative value indicates an antiferromagnetic interaction.

Complexes of binucleating ligands can be used to study the effect on the J value of changing the metal ion while the ligand system is kept constant. The following complexes have been used in this type of study [3]:



An increasing antiferromagnetic interaction was found for these complexes as the metal was varied from Mn(II) to Cu(II).

The effects of minor and major changes in ligation and coordination have also been studied as they affect magnetic exchange parameters. This can be done by either altering the back side of the ligand, the portion of the ligand not involved in bridging metal ions, or by altering the bridging unit itself. For example, Cu^{+2} and VO^{+2} complexes of the following ligand system were found to be particularly useful in this approach [4]:



The magnetic exchange parameter increases in magnitude for copper complexes as the R group is changed from electron-withdrawing to electron-donating groups, but decreases over the same range for the vanadyl complexes. This indicates a direct metal-to-metal exchange mechanism for the binuclear vanadyl complexes and a superexchange mechanism for the binuclear copper complexes of this ligand.

Coordination changes for complexes of the above ligand and for other similar systems at the bridging position X show some dramatic results. For example, a decrease is seen in the antiferromagnetic interaction as X = -OR is replaced with X = halide [5,6].

Multi-atom bridged systems exhibit similar characteristics [7]. These systems are also useful in determining the effect that lengthening of the bridging unit has on the intramolecular interactions. For one particular system, a magnetic exchange interaction is not seen experimentally with a biphenyl bridging unit, but it can be observed for the same system with a phenyl bridging unit [8].

Electrochemistry and Reactivity

Complexes of bisporphyrins exhibit metal-metal interactions [9,10]. Triplet state EPR spectra are observed for these complexes; this indicates a metal-metal intramolecular interaction. A direct through-space mechanism can best account for the observed results. One particular dicobalt(III) bisporphyrin complex has displayed catalytic behavior for the reduction of O_2 to H_2O [11].

Strong metal-metal interactions should promote interesting electrochemistry for binuclear metal complexes. The appearance of two one-electron reductions in a complex with interacting metal ions is a result of that interaction. Gagné et al. [12] take advantage of this property to synthesize a mixed-valence $\text{Cu}^{\text{II}}\text{-Cu}^{\text{I}}$ square planar complex of the ligand used in the metal ion series mentioned previously. This system has one unpaired electron and it is delocalized on the EPR time scale at room temperature. An examination of this same system at lower temperatures in solution shows that the seven-line hyperfine spectrum collapses to a four-line hyperfine spectrum characteristic of a localized species. This allows the calculation of an intramolecular electron transfer rate for this complex.

It appears that complexes of binucleating ligands can provide insights into the interactions between metal centers and that such interactions promote interesting electrochemistry and possible catalytic behavior in some of these systems.

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THE SYNTHESIS, REACTIVITY, AND ELECTRONIC CHARACTERIZATION
OF NEW LOW VALENT TITANIUM COMPLEXES

David R. Corbin

Final Seminar

December 11, 1979

Low valent complexes of titanium in the +2 and +3 oxidation states are of great interest because of their reactivity. Reduced titanium complexes are important in such reactions as Ziegler-Natta polymerization [1], nitrogen fixation [2], and olefin isomerization [3]. Despite this great reactivity, several titanium(II) complexes such as bis(η^5 -cyclopentadienyl)titanium dicarbonyl and bis(η^5 -cyclopentadienyl)titanium 2,2'-bipyridyl are found to be relatively stable. Studies of bis(η^5 -cyclopentadienyl)titanium bipyridyl have shown it to have a magnetic moment of 0.6 to 0.8 B.M. at room temperature. This weak paramagnetism exhibited by the complex is accounted for by a triplet excited state which is thermally accessible from the ground state singlet [4]. This interesting result has led to further investigations of exchange and electron transfer in various bis(η^5 -cyclopentadienyl)titanium systems bound to extended delocalized ligands [5].

Complexes of bis(η^5 -methylcyclopentadienyl)titanium(III) and bis(η^5 -cyclopentadienyl)titanium(III) to various substituted pyrimidines and related heterocycles have been prepared [6,7,8] and studied by EPR and variable temperature magnetic susceptibility [8,9]. In the case of the nucleic acid constituent uracil and its sulfur containing analogue, comparison of data shows unusual magnetic and EPR properties. The uracilate bridge leads to an antiferromagnetic interaction while the sulfur analogue exhibits a ferromagnetic interaction. Also, in the EPR a much larger zero field splitting parameter is observed for the sulfur containing complex. Low lying excited states involved in appreciable exchange interactions in the sulfur containing complex as well as slight structural changes from the oxygen to sulfur compounds may explain the unusual behavior. X-ray diffraction studies of 2,4-dithiopyrimidinobis[bis(η^5 -methylcyclopentadienyl)titanium(III)] were performed [7]. Additional studies have been conducted to investigate substitutional effects in the pyrimidine ring on the magnetic and EPR properties of a series of complexes. Complexes containing the dianions of dihydroxyquinoxaline and dithioquinoxaline as bridging units exhibit significant differences in the magnitude of the antiferromagnetic exchange interaction. The larger interaction in the sulfur analogue is accounted for through individual molecular orbital contributions in the exchange pathways [8].

Dicarboxylic acid complexes of bis(η^5 -cyclopentadienyl)titanium(III) with varying length aliphatic chains have also been studied [10]. Exchange interactions are observed to be propagated through the saturated system. Generally, upon increasing the saturated chain length, the magnetic exchange interactions decrease as well as the magnitude of the zero field splitting as observed in the EPR. Similar results are observed for the aromatic dicarboxylic acids. These results are in keeping with the proposal that a binuclear cobalt(III) complex, bridged by one carboxylate end of a dicarboxylic acid, is reduced by titanium(III) which complexes to the free end of the acid and transfers an electron through the carbon chain [11].

Several new complexes have been prepared in which intramolecular electron transfer is observed. Bis(η^5 -cyclopentadienyl)titanium phthalazine is a singlet molecule with a low-lying triplet excited state. Electronic and theoretical

studies support this. This complex has also been examined structurally [12].

Complexes of various substituted 1,10-phenanthrolines to bis(η^5 -cyclopentadienyl)titanium have also been synthesized and studied [13]. Generally, these systems exhibit electronic properties similar to those of bis(η^5 -cyclopentadienyl)titanium 2,2'-bipyridyl and bis(η^5 -cyclopentadienyl)titanium phthalazine. Fenske-Hall molecular orbital calculations support this observation. In the case of all the 4-methyl substituted 1,10-phenanthrolines complexed to the bis(η^5 -cyclopentadienyl)titanium moiety, electron transfer induced carbon-hydrogen bond dissociation is observed by mass spectral data and single crystal x-ray structure analysis. The single crystal x-ray structure was performed on bis(η^5 -cyclopentadienyl)titanium(4-methylene-3,7,8-trimethyl-1,10-phenanthroline). A second product bis(η^5 -cyclopentadienyl)titanium (4-hydro-3,4,7,8-tetramethyl-1,10-phenanthroline) was also isolated. Both these products exhibit doublet state EPR spectra as frozen glasses while the crystallizing solution shows a triplet state spectrum. A reaction mechanism is proposed to account for these and other observations.

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SYNTHESIS, CHARACTERIZATION, AND REACTIVITY
OF ELECTRON RICH TRANSITION METAL ORGANOMETALLIC COMPLEXES

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Final Seminar

December 11, 1979

Electron rich and coordinatively unsaturated organometallic species have been of considerable interest for sometime in the field of homogeneous catalysis [1]. These transition metal centers with enhanced basicity have been shown to allow the facile activation of C-H bonds [2]. One route to the generation of electron rich centers is via the use of organo lithium reagents. Interacting organo lithium reagents with transition metal hydrides generate transition metal-lithium bonded species, in effect an inorganic grignard reagent. It has been shown that the solubility and reactivity of these transition metal-lithium bonded complexes can be enhanced by use of chelating amines such as 1,1,4,7,7-pentamethyld ethylenetriamine (PMDT) [3].

The interaction of n-butyllithium with Cp_2MH_n ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{M} = \text{Mo}, \text{W}, \text{Re}, \text{Ta}$, $n = 1, 2, 3$) has generated transition metal lithium complexes that are typically very reactive but insoluble or react with common organic solvents [4]. The actual position of metalation on the transition metal hydride has been a point of discrepancy due to the inability to characterize the insoluble precipitates generated. Use of the chelating amine PMDT allows one to isolate an amine chelated transition metal-lithium complex which shows specific metalation at the transition metal leaving the Cp rings intact [5]. These reagents have proven to be useful in the synthesis of bimetallic complexes and the Cp_2Re monoalkyls [6].

The chemical shifts of protons bound to ligands coordinated to transition metals have been directly related to the amount of electron density present at the metal center. The increased amount of electron density present on the metal causes the proton resonances to shift to higher field [1]. The observed chemical shift of 5.82τ for the Cp ring protons of $\text{Cp}_2\text{ReLi}\cdot\text{PMDT}$ (I) indicate the generation of a very basic metal center. This is in comparison with the chemical shift of the protons on mono-Cp Re systems, recently reported at 4 to 4.65τ [7]. This extreme basicity of the Cp_2Re fragment accounts for the observation of "ligand scrambling" during the reaction of (I) with $\text{CpM}(\text{CO})_3\text{Cl}$ ($\text{M} = \text{Mo}, \text{W}$). The product of the reaction not only exhibited scrambling of ligands but also a set of semi-bridging carbonyls between the two different metal centers. These two semi-bridging carbonyls show extremely low stretching frequency in the infrared (1650cm^{-1} (Re-W), 1678cm^{-1} (Re-Mo)). The significant weakening of the C-O bond in the bridging carbonyls has been verified by x-ray diffraction studies of the Re-Mo bimetallic complex showing a lengthening of the C-O bond in the bridging carbonyls. The scrambling of ligands has also been observed for the reaction of (I) with $\text{Re}(\text{CO})_5\text{Br}$.

The Cp_2Re -mono alkyls exhibit more basicity than the parent compound(I). This is exemplified by the observation of the chemical

shift for the protons on the Cp rings at $\approx 6.1\tau$. This would indicate a possible wealth of chemistry available in the reaction of the Cp_2ReR with electrophiles. With this in mind the trityl cation, $\text{Ph}_3\text{C}^+\text{BF}_4^-$ was reacted with $\text{Cp}_2\text{ReCH}_2\text{CH}_3$ to yield $\text{Cp}_2\text{Re}^+(\text{CH}_2\text{CH}_2)\text{BF}_4^-$. Treatment of $\text{Cp}_2\text{Re-CH}_3$ with $\text{Ph}_3\text{C}^+\text{BF}_4^-$ generates an unsubstituted rhenium carbene, unstable at room temperature, which spontaneously rearranges to $\text{Cp}_2\text{Re}^+(\text{CH}_2\text{CH}_2)\text{BF}_4^-$. Treatment of Cp_2ReH with $\text{Ph}_3\text{C}^+\text{BF}_4^-$ allows one to isolate a lavender compound which reacts with acetone to form the yellow $\text{Cp}_2\text{ReH}_2^+\text{BF}_4^-$. Upon saturation of the reaction mixture with CO one can isolate analytically pure $\text{Cp}_2\text{Re}^+(\text{CO})\text{BF}_4^-$, which in itself is a very reactive species. Attempts to protonate the $\text{Cp}_2\text{Re-R}$ ($\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3$) with the acid HBF_4 causes the immediate evolution of RH , presumably through a very unstable transition metal alkyl hydride species. Treatment of Cp_2ReH with Magic Methyl ($\text{CH}_3\text{SO}_3\text{F}$) also results in the elimination of methane gas.

In conclusion, through the use of the very electron rich Cp_2Re fragment, we have been able to study the reactivity of C-H, C-C, and C-O bonds in close proximity to a basic organometallic transition metal center. These studies have allowed us to observe and study numerous types of transition metal bonding interactions (or functionalities) of importance in homogeneous catalysis [8].

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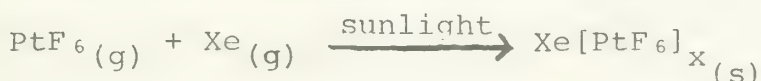
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SYNTHETIC AND STRUCTURAL CHEMISTRY OF XENON

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February 7, 1980

Bartlett and Lohman discovered that PtF_6 is a sufficiently strong oxidizing agent to oxidize O_2 . Since Xe has a lower oxidation potential than O_2 , and the predicted radius of Xe^+ is approximately the same as the radius of O_2^+ , Bartlett proposed that a thermodynamically stable Xe/PtF_6 compound could be prepared. In 1962 Bartlett successfully prepared the first xenon compound [1].



$$1 < x < 2$$

The subsequent preparation and characterization of xenon compounds through 1970 has been extensively reviewed [2]. These compounds, which are primarily xenon fluorides and xenon oxides, have structures that are nearly always well described by Valence Shell Electron Pair Repulsion Theory (VSEPR).

The structure of XeF_6 is not adequately described by VSEPR. The structures of gaseous, liquid, and solid XeF_6 are different. As a gas XeF_6 oscillates between C_{3v} and C_{2v} symmetry distorted octahedra [3]. As a liquid XeF_6 exists as a fluxional tetramer of XeF_5^+F^- units [4]. Tetramers plus hexamers of XeF_5^+F^- units constitute the lattice of solid XeF_6 [3]. These structures were determined on the basis of ^{19}F NMR, ^{129}Xe NMR, and x-ray crystallography.

Generally ^{129}Xe NMR is the best physical method for studying xenon compound structures. The ^{129}Xe nuclide has $I = \frac{1}{2}$, and Fourier-transform techniques must be employed due to the low gyromagnetic ratio [5].

One-electron-donors to xenon with high electronegativity are pseudohalogens, e.g. $-\text{OSeF}_5$ and $-\text{OTeF}_5$ [6]. Several xenon pseudohalogen compounds have been prepared by Seppelt, et.al. using a xenon fluoride in conjunction with a boron transfer agent [6,7,8,9].

The synthesis of a compound containing a Xe-N bond, $\text{FXeN}(\text{SO}_2\text{F})_2$, was reported in 1974 [10]. Xenon-129 NMR data suggests that $\text{FXeN}(\text{SO}_2\text{F})_2$ may be a fluxional molecule for which oxygen, not nitrogen, is bonded to Xe [5].

Preliminary evidence for the existence of a stable Xe-C bond was recently published [11]. Elemental analysis provides the primary support for the compound's existence. Decomposition during analysis is a major problem.

Xenon fluorides can be used as fluorinating agents of organic compounds. This application of xenon compounds has been reviewed [12]. Xenon compounds may also be applied to inorganic synthesis [13].

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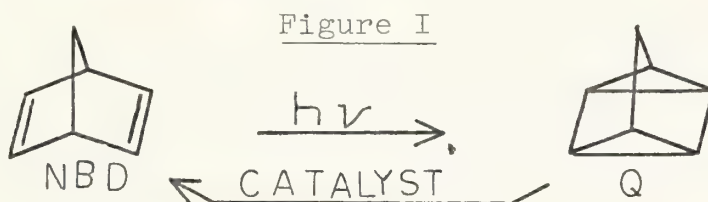
*Review

THE METAL CATALYZED INTERCONVERSION OF NORBORNADIENE AND QUADRICYCLANE

Edith Landvatter

February 12, 1980

Norbornadiene photoisomerizes to the highly strained tetracyclic compound quadricyclane.



Even though the strain energy of quadricyclane is estimated to be 96 kcal/mole [1], quadricyclane is thermally stable. The concerted thermal opening of quadricyclane to norbornadiene is symmetry forbidden by the Woodward-Hoffman rules. In the presence of a transition metal catalyst (for example $[\text{Rh}(\text{NBD})\text{Cl}]_2$ [2], cobalt tetraphenyl porphyrin [3], bis(acrylonitrile) nickel (0) [4], AgBF_4 [5] and others, the isomerization is rapid and exothermic.

Mechanism

Three mechanisms for this isomerization have been postulated. Mango and Schachtschneider propose a symmetry allowed pathway so that the rearrangement is concerted [6,7]. The metal d orbitals with the proper symmetry serve as a shuttle for the electrons. However, a concerted mechanism has not been proved for any catalyst in this system.

The second mechanism involves electrophilic attack of metal on carbon to form a metallocarbocation. The cation rearranges and extrudes the metal. This mechanism is indicated in the Ag (I) catalyzed rearrangements of cubane and quadricyclane [5,8].

A third mechanism proposes the oxidative addition of the metal to the strained bond forming a metallocycle which rearranges to reductively eliminate the norbornadiene. Evidence for this mechanism is inferred in the stoichiometric trapping of a Rh metallocycle using $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ [9]. A recent paper reports the spectroscopic detection of a Rh(III) complex and the observation of rhodocyclobutanes by low temperature NMR in the reaction mixture using $[\text{Rh}(\text{NBD})(\text{ACO})]_2$ as the catalyst [10].

Photoisomerization

The photoisomerization of norbornadiene occurs in the presence of triplet sensitizers such as acetophenone. Other sensitizers for this reaction are Cu(I) halides and phosphines. The copper halide salts form a copper-norbornadiene complex which is photoactive [11]. The copper phosphines react by a different pathway. The copper

phosphine forms a photoexcited complex which reacts with the norbornadiene through an electronic energy transfer or an excited state complex [12].

Solar Energy Storage System

This interconversion is being investigated as a possible solar energy storage system. The quadricyclane-norbornadiene isomerization is highly exothermic, giving off ~240 cal/g. Research is in progress to find catalysts to improve the quantum efficiency of the photoisomerization. Other groups are working on polymer bound catalysts [13, 14] for the development of an efficient energy storage system.

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TWO-DIMENSIONAL NMR - INORGANIC APPLICATIONS

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February 14, 1980

Two-dimensional NMR spectroscopy has developed rapidly during the last decade. Although most of the work has centered about ^1H and ^{13}C NMR, recent investigations involving ^{31}P and ^{11}B have more of an "inorganic" flavor to them [1-3]. "2D" experiments are characterized by a two-dimensional array of time domain data $[s(t_1, t_2)]$ which is converted to the frequency domain $[s(\omega_1, \omega_2)]$ by consecutive Fourier transformations [4-6]. While multiple-pulse techniques form the basis for all "2D" experiments, interesting and useful variations can be obtained by modifications in the basic pulse sequences.

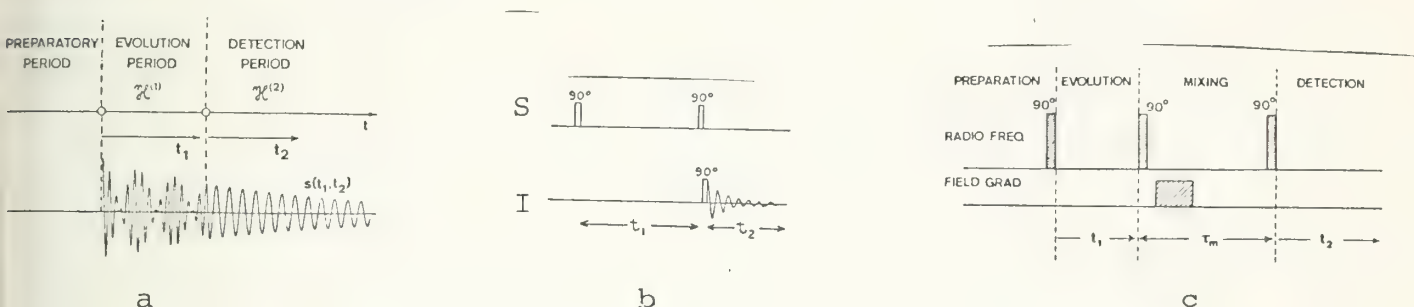


Figure 1

Extensive spectral simplification, as well as homonuclear coupling constants (J), can be obtained by means of "2D" J-resolved spectroscopy (Figure 1a), which is based upon the spin-echo pulse technique [4-10]. A 90° pulse generates transverse magnetization, which will dephase into components of differing frequencies due to field inhomogeneity, chemical shifts, and spin-spin coupling. A 180° pulse at time τ will then refocus the spin isochromats into a spin-echo at a time 2τ after the 90° pulse. If homonuclear spin-spin coupling is present, the refocusing will be incomplete and the echo will be modulated as those isochromats, corresponding to the spin multiplets, come into and out of phase. A Fourier transformation according to t_2 will give information concerning chemical shifts, yielding a "broad-band decoupled" spectrum projected onto the ω_2 axis. Appropriate cross-sections taken parallel to the ω_1 axis would yield individual spin multiplets, from which J could be measured.

Heteronuclear "2D" NMR spectroscopy (Figure 1b) can be used to obtain information on a "localized" portion of a spin population S which is coupled to a spin system I [1-3,11]. The initial 90° pulse will generate transverse magnetization for S . A second 90° pulse at time t_1 will lead to nonequilibrium population of the energy levels for S , and a 90° pulse of I will then lead to a free induction decay (FID) which contains information only about those S nuclei which are coupled to I nuclei. In this way, I (eg. ^{31}P or ^{11}B) can be used to "label" a specific portion of the S population (eg. ^1H).

A third type of "2D" spectroscopy is that used to follow exchange phenomena (Figure 1c) [12]. A 90° pulse produces transverse

magnetization, whose components dephase for t_1 before a second 90° pulse rotates them back to the z axis. These modulated z components form the initial conditions for the exchange process which takes place over a time τ_m . A third 90° pulse then produces observable transverse magnetization and the resulting FID is recorded over t_2 . Due to the frequency labeling of the magnetization components, they can be followed throughout the exchange process and the pathway can thus be determined. The precession frequencies during the evolution process transform as ω_1 , and ω_2 represents the precession frequencies during the detection period.

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PHOTOCHEMICAL WATER SPLITTING

James Goodale February 19, 1980

The need to convert solar energy into a storable form of electrical energy has provided the impetus for current research in photochemical water splitting [1]. Transition metal compounds may play several roles in the photogeneration of hydrogen and oxygen from aqueous media, including that of photosensitizer, oxidative or reductive quenching agent, or redox catalyst.

A number of metal salts may undergo photoredox chemistry in acidic solutions to yield hydrogen [2]. Recent work with the $\text{Cu}^{\text{I/II}}$ couple indicates that a solvated electron is produced via a charge transfer to solvent absorption band [3]. Gray and co-workers have succeeded in producing hydrogen from concentrated aqueous solution of HCl, using a rhodium(I) dimer $[\text{Rh}_2(\text{bridge})_4]^{2+}$, where bridge = 1,3-diisocyanopropane [4].

Trisbipyridyl ruthenium(II) cation $[\text{Ru}(\text{bpy})_3]^{2+}$ is thermodynamically capable of oxidizing or reducing water in its triplet MLCT excited state [5,6], however, these reactions are not favored kinetically. Current studies, using $[\text{Ru}(\text{bpy})_3]^{2+}$ as a sensitizer, have resulted in several interesting procedures for oxidative or reductive quenching, such that the photoinduced evolution of hydrogen and oxygen is possible [7-12]. A typical method would be to use a reductive quenching agent to convert the excited $^*\text{Ru}(\text{bpy})_3^{2+}$ to $[\text{Ru}(\text{bpy})_3]^+$, and then to use an electron acceptor to restore the sensitizer to the original oxidation state. Then the acceptor species may reduce water to hydrogen in the presence of an appropriate catalyst, such as colloidal Pt.

The photochemical cleavage of water has also been achieved by employing metal exchanged zeolites. Hydrogen and oxygen are produced by titanium(III) and silver(I), respectively [13-15]. The choice of zeolite is important in terms of quenching properties and robustness of the zeolite lattice. Unfortunately, the cations in zeolites must be thermally restored to an oxidation state that gives rise to the photolysis of water. There have been claims of other heterogeneous systems, such as glass supported monolayers of surfactant derivatized $[\text{Ru}(\text{bpy})_3]^{2+}$ and also metal oxides (TiO_2), that would split water, but these claims have not been borne out in subsequent work.

Recent developments with photoelectrode semiconductors has allowed the cleavage of water in homogeneous solutions of electrolytes with zero applied bias potential [16]. SrTiO_3 and KTaO_3 are particularly well suited for this application since their conduction band potential is just a few tenths of a volt above the H_2/H^+ potential. Thus there is enough band bending to allow efficient current flow at photoequilibrium. In addition, the use of platinized metal oxide semiconductors reduces the hydrogen overvoltage and allows for "short-circuit" redox chemistry. This catalytic action

is also observed for palladium, nickel, or copper on p-type or n-type electrodes [17,18].

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MACROCYCLIC LIGANDS AND THE TEMPLATE EFFECT

John E. Hoots

February 21, 1980

Introduction

Macrocyclic compounds represent an important class of ligands and interest in them has been growing at an accelerating rate. A macrocyclic ligand is a ring(ed) structure containing three or more donor atoms available for coordination with each metal center [1]. Some of the major classes of macrocycles are:

- 1) "Crown" polyethers
- 2) S and N-substituted "crown" compounds
- 3) "Crown" compounds w/o "O" donor atoms
- 4) Compounds unsaturated at "N" donor atoms
- 5) Phthalocyanines
- 6) Porphyrins
- 7) Corrins
- 8) Binucleating compounds

A structural example of each of them appears on page four. Macrocyclic ligands have many important applications. For example, porphyrin and corrin complexes have received much attention as models for important biological molecules such as hemoglobin, chlorophylls, cytochromes, and vitamin B₁₂ [2]. Phthalocyanine complexes have been studied as oxidation catalysts [3] and are a very important class of industrial pigments [4]. Crown polyethers have been researched as possible therapeutic agents to selectively remove radioactive Sr²⁺ from humans [5] isotopic enrichment of certain Group IA and IIA elements, and to solubilize ionic compounds in non-polar solvents [6]. Binucleating macrocycles have received attention as models for biological enzymes such as nitrogenase, and in studies to investigate the chemistry of two interacting metal centers [7]. The applications of macrocyclic ligands are numerous and interest will undoubtedly grow in the future.

Synthesis

The synthesis of macrocyclic ligands generally utilizes bifunctional reagents in such organic reactions as nucleophilic substitutions [8] and Schiff-base condensations [9]. Occasionally, more complicated types of reactions are required, but these mainly involve syntheses of porphyrins and corrins [4]. Several major problems are associated with cyclization reactions. The most common one is polymerization or oligomerization of the reactants [10], and it has represented a major barrier to the synthesis of macrocyclic ligands. Reactions are sometimes carried out at high dilution in order to decrease the probability of the reactants coming together in a linear fashion (to form a polymer) and to promote cyclization [11]. Another technique involving the introduction of a metal ion into the reaction mixture, has met with much success [11].

The "Template Effect"

The mechanism by which the metal ion acts was first investigated by E. L. Blinn, D. H. Busch, and M. C. Thompson. They formulated the concept of the "kinetic template effect" whereby the coordination sphere of the metal ion holds the reactive groups of the reactant(s) in the proper spacial positions for a cyclization reaction to occur [11]. Usually, the best metal "templates" are believed to possess the proper coordination geometry to enhance cyclization [11] and to tightly coordinate the reactant(s) [12].

There have been several attempts to "prove" the template effect for certain selected systems. These have led to mixed results [12,13,14]. A major stumbling block is that the mechanisms for most cyclization reactions (in the presence of metal ions) are exceedingly complex. Also, paramagnetic coordination complexes are often present which severely limit the use of NMR to study even simple systems [11].

However, as a synthetic tool, the use of metal ions has been invaluable, and the label "template reaction" has been applied (and occasionally misapplied) to almost every reaction where enhanced yields of macrocyclic ligands have been observed. In addition to the synthesis of new types of macrocyclic ligands [15], many new investigations as to how metal ions affect cyclization reactions have been completed recently. The synthesis of large-ring binucleating macrocycles have shown that metal ion size has a significant effect [16]. The synthesis of "superphthalocyanines" has indicated that metal ion size, coordination number, and metal-donor atom bond lengths can all play a role in cyclization reactions [17]. There has been an effort to show that the biological synthesis of macrocyclic ligands may involve a "template effect" of non-transition elements such as Mg^{2+} [18]. Originally, Ni^{2+} and Cu^{2+} were used extensively as templates and gradually the list of metal ions which have been used has grown. Presently, researchers are trying to extend the list of metal ions to such "unusual" species as Sc^{3+} and Ru^{3+} [19,20]. Finally, in response to the unanswered questions about cyclization mechanisms, some progress has been made in trapping reaction intermediates in template reactions [21]. Much work is being done in this interesting field of coordination chemistry and it appears future work will delve even deeper into the concepts and ideas presented in this abstract.

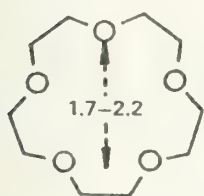
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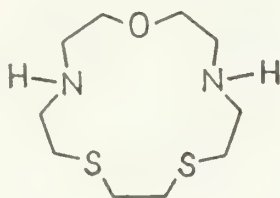
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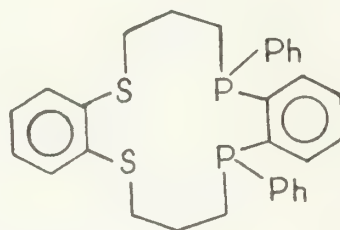
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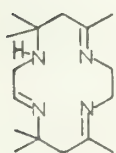
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polyether



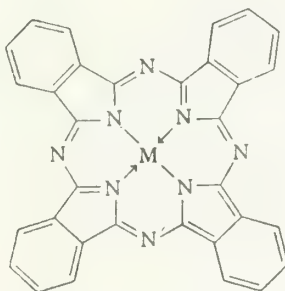
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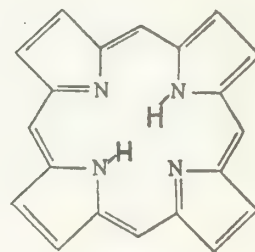
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w/o "O"



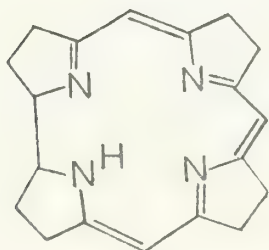
Unsaturated
at "N" donors



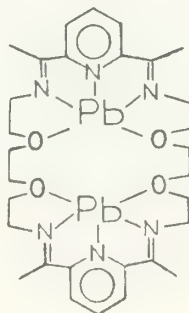
Phthalocyanines



Porphine



Corrins



Binucleating

TRIPLE DECKER SANDWICH COMPLEXES

Debra Wroblewski

February 26, 1980

A wide variety of triple decker sandwich complexes has been synthesized in recent years [1,14,15]. The triple decker structure consists of a bridging ligand "sandwiched" between two metals each of which have additional terminal ligands. The term "triple decker" was originally introduced by Cotton and Wilkinson in 1954 pertaining to an erroneously proposed structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3]_2$ $\text{M} = \text{W}, \text{Mo}$ [2,3]. Schumacher and Taubenest detected the first triple decker sandwich structures in the mass spectrum (20eV) of ferrocene and nickelocene revealing $\text{Ni}_2(\text{Cp})_3^+$, $\text{Fe}_2(\text{Cp})_3^+$ and $\text{NiFe}(\text{Cp})_3^+$ [4].

In 1972 Werner and coworkers isolated the first triple decker transition metal compound while attempting to model the electrophilic substitution reaction of ferrocene [5]. Nickelocene was chosen as the system to model this process because the proposed intermediate $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\eta^4\text{-C}_5\text{H}_5\text{E})]^+$ would be a stable 18 electron species for $\text{M} = \text{Ni}$, as opposed to an unstable 16 electron species for $\text{M} = \text{Fe}$. This led to the reaction of Ph_3CCl which produced a substituted cyclopentadiene and NiCl_2 for which Werner has proposed a mechanism [1]. In order to trap the proposed intermediate, Werner later used a non-coordinating anion which yielded the triple decker cation, Ni_2Cp_3^+ . This species is very air sensitive and reacts readily with Lewis bases to cleave the inner ring from one of the nickel atoms. This results in the removal of a "story" from the triple decker sandwich. Werner has proposed a reaction sequence for the formation of Ni_2Cp_3^+ from NiCp_2 and HX ($\text{X} = \text{BF}_4$) based on the site of proton attack on nickelocene. This site of attack has been elucidated by an NMR study using isotopic labeling [6].

In order to better understand the bonding in the triple decker sandwich structures, R. Hoffmann and coworkers carried out a molecular orbital treatment of this particular class of compounds [7]. Hoffmann relies on fragmentation analysis which is based on the partitioning of the molecule into smaller subunits of well characterized valence orbitals. The resulting molecular orbital diagram, based on extended Huckel calculations, indicates that both 30 and 34 valence electron triple deckers should exhibit thermodynamic and kinetic stability.

Triple decker complexes containing a heterocyclic bridging ligand are also well known. R. N. Grimes and coworkers have worked on the synthesis and characterization of cobalt triple decker carboranes [8] which are very air stable, in contrast to the Ni_2Cp_3^+ species. Grimes has done work on the unusual synthetic and structural aspects of these species while Geiger has studied their electrochemical properties [9]. Another heterocyclic bridging ligand, diborolene, has been synthesized by Siebert and coworkers [10]. Their work has produced a number of paramagnetic mixed metal sandwich complexes containing from 31-33 valence electrons. In addition Siebert has done work using the thio-diborolene ligand [11] to produce a 30 electron triple decker $(\text{C}_2\text{H}_5)_2\text{Fe}_2(\text{C}_2\text{B}_2\text{SR}_4)$.

Recently Geiger and coworkers have reported the electrochemical generation of $(\text{CpCo})_2\text{COT}^{2+}$ (COT = cyclooctatetrene) which is isoelectronic with Ni_2Cp_3^+ [12]. This dication species is produced by a reversible two electron oxidation of $(\text{CpCo})_2\text{COT}$, which is a 36 electron species. Skell and coworkers have studied yet another variation on the triple decker structure, tris(cyclooctatetrene)dititanium [13]. Reduction of this paramagnetic neutral complex with potassium produced a solution of the diamagnetic 34 electron $(\text{COTTi})_2\text{COT}^{2-}$ anion.

A large number of triple decker sandwich complexes incorporating many different transition metals have been synthesized which are structurally and electrochemically interesting. Possible future work in this area would include synthesis of other triple decker complexes by oxidation or reduction of multimetallic π compounds or by synthesis of new π -ligands to bridge the two metal centers.

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Group VIII Metal Complex Activation of O₂ Towards Organic Substrates

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February 28, 1980

A large variety of transition metals catalyze the oxidation of organic substrates with hydroperoxides, water, or dioxygen. Many group V and VIB metal complexes specifically catalyze the epoxidation of olefins with ROOH [1]. The Smidt reaction (Wacker process) utilizes dioxygen as the oxidant in the formation of aldehydes and ketones from olefins; however, water is the actual reagent involved in these oxidations catalyzed by PdCl₂ or RhCl₃ [2,3]. Group VII, VIII and IB metal complexes in general are good ROOH decomposition catalysts, forming free radicals via the Haber-Weiss mechanism [4]. Metal complex catalyzed oxidations with dioxygen almost always proceed through free radical intermediates—but initiation may occur in several ways [5].

In the last fifteen years quite a number of metal-dioxygen complexes have been synthesized. Many were reported to react with small inorganic molecules via direct oxygen atom transfer mechanisms, resulting in metal-bound, or free, oxidized products [6]. Several of these reactions are catalytic. Stoichiometric reactions with several organic substrates have also been reported [6], yielding metallocyclic complexes of oxidized substrates.

It has only been in the last six years that evidence for catalytic, metal-centered oxidations of organic substrates with direct oxygen atom transfer from O₂ have been reported. The first of these was the oxidation of styrene catalyzed by several Rh(I) species [7]. It was found that the presence of a free radical inhibitor had no effect on the formation of the major product, acetophenone, but did reduce the quantity of benzaldehyde (cleavage product) to approximately 25% its level without an inhibitor. Known free radical initiators produce predominantly styrene oxide and polyoxide. The acetophenone formation rate was found to be independent of the water concentration, indicating a Wacker-type cycle is not operative. This was further evidenced by tracer studies using H₂¹⁸O. The catalytic oxidation of 1-octene in the presence of excess triphenylphosphine by Wilkinson's catalyst resulted in the formation of 2-octanone, heptanal and triphenylphosphine oxide [8]. Free radical and Wacker-type pathways were ruled out in this study as well.

The synthesis and characterization of a variety of metallocyclic peroxo-olefin complexes from O₂ and electrophilic olefins was reported for Pt, Pd, Rh and Ir phosphine complexes [9]. These were characterized by ¹H and ¹³C NMR. The cyclic adducts could be thermally decomposed, yielding ketones (or aldehydes) resulting from cleavage of the double bond. This study lends further credence to proposal of a metal-centered oxidation of olefins in some systems. Similar mechanisms have been proposed for benzaldehyde [10] and cyclooctene [11] oxidations. Most recently a rhodium catalyzed oxidation of terminal olefins to methyl ketones, with and without the presence of a CuCl₂ co-catalyst, was reported [12]. The evidence points to a process which may be thought of as a coupled

Wacker process, and leads to the proposal of a mechanism fundamentally similar to those presented by the earlier workers in this field.

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Recent Organo-lanthanide and -actinide Chemistry

Paul F. Schubert

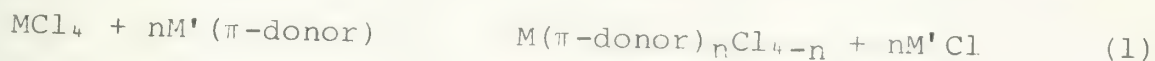
March 6, 1980

Interest in the organometallic chemistry of the f-elements is a natural extension of research into similar complexes of the transition metals. It is believed that the number, energy, and spatial arrangement of the f-orbitals will allow catalysis of reactions which cannot be catalyzed by other metals.

Although Wilkinson synthesized several organo-lanthanides and actinides in 1956 [1], it was not until Streitwieser's synthesis of uranocene in 1968 [2] that any systematic research into the structure and reactivity of organometallic f-element complexes was undertaken. The development of this field is well covered in several recent reviews [3].

Evans et al. [4] have recently reported the vapor phase synthesis of several low coordinate complexes of the form $\text{Ln}(\text{C}_4\text{H}_6)_3$ [$\text{Ln} = \text{Er}, \text{Nd}, \text{Sm}$], and $\text{Ln}(\text{Me}_2\text{C}_4\text{H}_4)_2$ [$\text{Ln} = \text{Er}, \text{La}$], the latter being the first known paramagnetic complex of lanthanum. The nature of the metal-carbon interaction is poorly understood. A novel complex containing an η^8 - η^2 bridging cyclooctatetraene has recently been synthesized in the vapor phase by DeKock et al. [5]. The carbons that serve as bridges between the two neodymiums in $[\text{Nd}(\text{COT})(\text{THF})_2][\text{Nd}(\text{COT})_2]$ appear to be π bound to both metals.

The π complexes of the actinides form a large class of the f-element organometallic compounds. Synthesis of these compounds is typically by means of a transmetallation reaction as shown in equation (1). Compounds with substituted π donors, such as

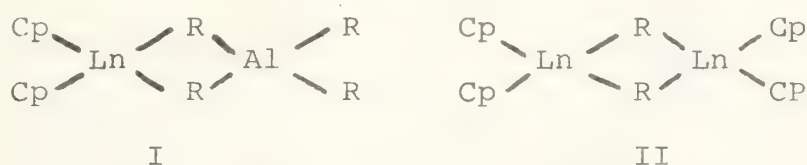


$\text{M} = \text{U}, \text{Th}$ $\text{M}' = \text{Li}, \text{Na}, \text{Tl}$ $\pi\text{-donor} = \text{allyl}, \text{Cp}, \text{COT}, \text{etc.}$

butenouranocene [6], are generally prepared by synthesis of the donor with its substituent attached before the complex is formed. A substituted cyclopentadienyl complex of uranium with a magnetic non-equivalence for the cyclopentadienyl protons has recently been prepared by Dormond and Duval [7]. This inequivalence is attributed to the prochirality of the uranium atom.

Marks recently [8] sought to isolate and characterize two compounds, Cp_2UCl_2 and CpUCl_3 , which would be less coordinatively saturated than most π actinides. In their investigation of Cp_2UCl_2 , they determined on the basis of spectral evidence that Cp_2UCl_2 is misformulated, and is actually a mixture of Cp_3UCl and CpUCl_3 . A crystal structure of the THF adduct CpUCl_3 was performed in conjunction with this research. Marks has also recently reported the synthesis of a Cp_2UCl trimer [9], which serves as a route to several other organo-actinide compounds. π Complexes of the lanthanides can also be prepared, but recent years have seen little work of interest, Schumann's synthesis of organometallics containing a Ln-Ge or a Ln-Sn bond [10] and Raymond's synthesis of a pyrazine bridged Cp_3Yb dimer [11] being the prime exceptions.

There has been little current research on compounds containing both π and σ M-C bonds for the actinides, but recent work by Holton and Lappert [12,13] into analogous lanthanide compounds has produced results of some significance. They have synthesized several alkyl bridged bimetallic complexes of the type illustrated below.



These complexes are similar to structures proposed as the catalytic species in Ziegler-Natta type olefin polymerization reactions [14], and have been found to catalyze the polymerization of ethylene to polyethylene [15]. These catalysts produce polymers with molecular weights in the range of 10^3 to 10^4 daltons. The lifetime of the catalyst is lanthanide and temperature dependent, and is generally less than three hours.

Peralkyl lanthanides, LnR_n [$\text{R} = \text{CH}_3, \text{CH}_2\text{Si}(\text{CH}_3)_3$] have been synthesized by Schumann [16] using alkyl lithium reagents. These compounds are relatively stable thermally, although like almost all f-element organometallics they are extremely oxygen and moisture sensitive. Deacon et al. [17] have synthesized several peralkyl species, R_2M [$\text{R} = \text{PhC}\equiv\text{C}$, or fluorenyls] which have been characterized by physical and chemical means. Peralkyl actinides have not been reported.

The synthesis of actinide hydrides has been reported by both Marks [18] and Anderson [19]. Marks has prepared compounds of the form $\{\text{M}[(\text{CH}_3)_5\text{C}_5]_2\text{H}_2\}_2$ where $\text{M} = \text{Th}, \text{U}$. NMR and IR data suggest the presence of two bridging and two terminal hydrides for this dimeric species. Anderson has synthesized a monomeric monohydride of the form $\text{HM}[\text{N}(\text{SiMe}_3)_2]_3$ where $\text{M} = \text{Th}, \text{U}$, which is observed to undergo complete exchange of all of the hydrogens for deuterium through a proposed metallocycle intermediate [20]. Lanthanide hydrides have not been reported.

The last few years have seen a great expansion in the known organometallic chemistry of the f-elements. Of prime importance has been the identification of an alkyl-bridged lanthanide as the catalytic species in a Ziegler-Natta type polymerization. The preparation of actinide hydrides has also been significant, as it confirms the existence of species which play important roles in transition metal catalysis. However, the absence of peralkyl actinides and organometallic lanthanide hydrides cause significant gaps in the knowledge of f-element organometallics.

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The Chemistry of S_4N_4

David Lesch . March 11, 1980

Tetrasulfur tetranitride was first prepared in 1835 by the reaction of disulfur dichloride with ammonia. Early elucidation of its chemistry was, perhaps, hindered by the tendency of S_4N_4 to explosively eliminate N_2 . Recent interest in S_4N_4 and its derivatives stems from the unusual properties and structures exhibited by these compounds.

S_4N_4 forms thermochromic crystals in which the eight membered rings have a realgar structure. Four nitrogen atoms occupy a square plane with a distorted tetrahedron of S atoms superimposed. (D_{2d} symmetry). This structure was rationalized by Gleiter in 1970 via symmetry arguments and extended Hückel calculations [1].

Reaction of S_4N_4 with many metal halides and carbonyls in alcohol produces $M(S_2N_2H)_2$ in which $-SNSN(H)-$ functions as a bidentate ligand [2]. S_4N_4 can also function as a source of sulfur or nitrogen in the preparation of $(PhCHN)_2Sx$ and $(NPCl_2)_3$ from $PhCH_2NH_2$ and PCl_3 , respectively. In a novel one step synthesis Tashino et al., in 1977, prepared benzobis- and benzotris[1,2,5]thiadiazole from S_4N_4 and alkoxybenzenes [3].

S_2N_2 , which is produced by the catalytic cleavage of S_4N_4 vapor on Ag wool, can be thermally polymerized to metallic polysulfur nitride $((SN)_x)$. X-ray structures show $(SN)_x$ to be parallel chains of alternating S-N atoms arranged in fibers [4]. In 1973 Labes et al. measured the conductivity of a single crystal of $(SN)_x$ and found it to be metallic from 4.2-300°K. Three years later Street et al. reported that $(SN)_x$ became superconducting along the fiber axis at 0.3°K. Physical measurements indicate that $(SN)_x$ is a highly anisotropic 3-D semimetal. Recently bromination of $(SN)_x$ has produced crystals with increased room temperature conductivity.

In 1979 Gebauer et al. reported the isolation of $S_4N_4Cl_2$ by the careful reaction of Cl_2 with S_4N_4 [5]. This compound served as a precursor for the preparation of bicyclic S_4N_4Cl and S_5N_6 by Chivers et al. [6] and Roesky et al. [7], respectively. Chivers also found that reaction of S_4N_4 with MN_3 can lead to the formation of either $S_3N_3^-$ or $S_4N_5^-$ depending on the cation. He has suggested that these two anions play a central role in the reduction of S_4N_4 [8].

Banister et al. have recently characterized a large number of adducts formed from reaction of Lewis acids with S_4N_4 in inert solvents. The structure of the S_4N_4 moiety in these adducts can range from that of free S_4N_4 to a nearly planar ring [9].

Adjacent S atoms in S_4N_4 can add across $C=C$ double bonds to form stable cyclic compounds. Subsequent photolysis has been shown by Ingold et al. to yield long lived dithiazolidine radicals [10]. The mechanism which leads to these radicals and to the above mentioned cyclic SN compounds is a topic of much current research.

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The Photochemical Reaction of $\text{Re}_2(\text{CO})_{10}$
With H_2O and Related Systems

David Gard

March 12, 1980

In 1975, Herberhold and Süß discovered that $\text{Re}_2(\text{CO})_{10}$ is converted under photolysis in aqueous ether solution to the tetranuclear hydroxo complex $[\text{Re}(\text{CO})_3\text{OH}]_4$ with evolution of H_2 (reaction (1)) [1]. Few stable metal hydroxocarbonyl complexes are known,



and their formation is rather novel in light of the established chemistry of metal carbonyls with H_2O . This reaction was examined to determine the processes involved in the photochemical activation of the water molecule by a metal carbonyl.

Irradiation of $\text{Re}_2(\text{CO})_{10}$ in aqueous THF with 366 nm light confirmed that $[\text{Re}(\text{CO})_3\text{OH}]_4$ is the final quantitative product but the reaction proved to be much more complex than originally reported. The intermediacy of the aqua substituted complexes $\text{eq-Re}_2(\text{CO})_9(\text{OH}_2)$ and $\text{dieq-Re}_2(\text{CO})_8(\text{OH}_2)_2$ has been established. The mono-aqua complex, which is quite light and medium sensitive, is formed as the only product of the photoreaction if 313 nm light is used. Quantum yield measurements demonstrate a dependency on $[\text{CO}]$ and on light intensity, indicating that formation of $\text{eq-Re}_2(\text{CO})_9(\text{OH}_2)$ occurs predominately via a pathway involving dissociative substitution of CO at photogenerated $\text{Re}(\text{CO})_5\cdot$ free radicals.

Under 366 nm irradiation $\text{eq-Re}_2(\text{CO})_9(\text{OH}_2)$ initially yields $\text{Re}_2(\text{CO})_{10}$, $\text{HRe}(\text{CO})_5$, and $[\text{Re}(\text{CO})_3\text{OH}]_4$. It is proposed that photo-induced homolysis results in disproportionation to $\text{Re}_2(\text{CO})_{10}$ and the unobserved $\text{dieq-Re}_2(\text{CO})_8(\text{OH}_2)_2$. This latter complex may rapidly dissociate H_2O , allowing addition of the coordinated water molecule to occur across the Re-Re bond, followed by elimination of $\text{HRe}(\text{CO})_5$ to yield $[\text{Re}(\text{CO})_3\text{OH}]_4$. $\text{HRe}(\text{CO})_5$ may form other hydrides under the reaction conditions, but under continual photolysis all rhenium species are converted to $[\text{Re}(\text{CO})_3\text{OH}]_4$ and H_2 . Also present at intermediate stages of the reaction is a red ionic product formed in very low yield.

Thermal attempts to prepare $\text{dieq-Re}_2(\text{CO})_8(\text{OH}_2)_2$ from $\text{dieq-Re}_2(\text{CO})_8(\text{CH}_3\text{CN})_2$ and H_2O also yield $[\text{Re}(\text{CO})_3\text{OH}]_4$, confirming that the bis-aqua complex is a precursor for oxidative addition. The addition of substrates across the metal-metal bond has not previously been recognized as a general reaction mode for dinuclear group VII metal carbonyls. The similarity to the lightly stabilized $\text{Os}_3(\text{CO})_{10}\text{L}_2$ ($\text{L} = \text{CH}_3\text{CN}$, cyclooctene) complexes which easily undergo oxidative addition of a variety of hydrogen containing compounds may be noted [2].

The chemistry of dinuclear rhenium carbonyl complexes substituted with nitrogen donor bases has also been studied. A case

in point is demonstrated by the 366 nm photolysis of eq-Re₂(CO)₉(py) or dieq-Re₂(CO)₈(py)₂ (py = pyridine) in THF. In either case, the same products are formed: Re₂(CO)₁₀, Re(CO)₃(py)₃⁺, HRe₄(CO)₁₆⁻, and HRe₂(CO)₇(py)(o-pyridyl). These compounds are stable analogs of the intermediates proposed above for reaction (1) and their formation is best explained by facile competitive dissociation of pyridine or CO from photogenerated Re(CO)₄(py)•.

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Electron Energy Loss Spectroscopy and its Applicability to Inorganic Systems

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March 13, 1980

Necessity often brings new techniques into the vast scope of chemical analyses and so it is with electron energy loss spectroscopy (ELS). Until the development of this technique, surface studies from vibrational spectra had to be obtained with tunnel spectroscopy and infrared adsorption spectroscopy. Unfortunately, these techniques did not allow extrapolation from the experimental results to surface species involved in catalytic systems [1].

ELS results from the inelastic scattering of an electron beam from a surface, with a subsequent transfer of energy to the surface. This loss of energy is monitored by analyzing the scattered electron beam. The approaching electron induces an image charge in the metal, resulting in an electric field between the electron and the image charge. For surfaces with high dielectric constants, this electric field is perpendicular to the metal surface for the same reason as it is in IR reflection spectroscopy [5]. The electric field can then excite vibrational surface modes if the oscillating dipole has a component normal to the surface. This result is the so-called "Surface Selection Rule" for both ELS and IR reflection spectroscopy [2,3,4,5]. The predominant interaction originates when the electron is far from the surface, giving rise to an electric field that is nearly homogeneous at the surface, on an atomic scale. This is true as long as the energy of the incident electron is at least ten times greater than the loss energy [5].

Loss energies of primary interest range from 0-40eV [6], resulting in both vibrational and electronic information about the system. Resolution is limited to 7-150meV [3] due to the difficulty in establishing a truly monochromatic electron source. The sensitivity is relatively high, with a 1/1000 monolayer of CO easily detected [1].

Luscher and Propst have studied the adsorption of O₂ onto W(100), (see Kittel for an explanation of the nomenclature) and its reactivity. From the investigations, they observed two nonequivalent binding sites for oxygen and an absence of molecular oxygen on the surface. The binding energies of these two states could be ascertained. The vibrational spectra of this system were studied [9], and five distinct phases of adsorption were observed which led to a model for oxygen coverage on W(100). From these examinations it was demonstrated that O₂ dissociated on adsorption, two distinct binding sites existed, and surface coverage occurred in a five-step, sequential manner. Rieder has observed O₂ adsorbed on Nb(110), but the results were only tentative.

Methanol adsorbed on Ni(111) resulted in O-bound methanol, which converted to a methoxy species on heating and finally decomposed to adsorbed CO and O with further heating [11]. Ultra-violet photomission spectroscopy confirmed these results [12].

C_2H_2 and C_2H_4 adsorbed on Pt(111) have been observed with subsequent conversion to a new surface species at 300K [1,13], the nature of which is still in dispute [15]. On additional heating of adsorbed C_2H_2 to 450K, the appearance of CH species on Ni(111) has been monitored [14]. These observed reaction intermediates, their characterization, and eventual application in formulating catalytic pathways are a significant step to understanding catalysis.

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*Review

Silica Supported Chromium Catalysts for Olefin Polymerization

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March 20, 1980

The catalytic polymerization of olefins is of major industrial importance [1]. The use of supported chromium oxide to make high density polyethylene from ethylene (Phillips process) was the first commercially feasible use of a heterogeneous catalyst in this reaction [2]. The most recent review dealing with these catalysts was published in 1969 [3].

Although the Phillips catalyst has been known for 30 years, a detailed knowledge of the active site, as for most heterogeneous catalysts, is not yet at hand. Conventional methods of study such as physis- and chemisorption of gases [4] and temperature programmed reduction [5] are not always very informative. The trend today is thus toward increased use of spectroscopic techniques [6].

The Phillips catalyst is generally prepared by impregnating silica gel with an aqueous solution of CrO_3 . The catalyst is then dried, calcined, and finally reduced before use. Impregnation and the subsequent calcination is believed to result in the formation of a surface-stabilized chromate [7] or dichromate [8] species. The stability of these species has been shown to be acutely dependent on water content, Cr loading, and calcination temperature [9]. For example, x-ray photoelectron spectroscopy has shown clearly that for catalysts of medium (>5%) loading, a high calcination temperature causes formation of $\alpha\text{-Cr}_2\text{O}_3$ [10,11].

To become active, the Phillips catalyst must be reduced. The nature of the reduced catalyst is much less well understood, but it is clear from Electron Paramagnetic Resonance that the chromium exists in several oxidation states on the surface [3]. The oxidation state of the active site is a matter of some controversy [12]. However, the reduced catalyst contains considerable amounts of Cr(II) [13] and Krauss has shown that the catalyst activity is linearly related to Cr(II) content [14]. As in the calcination step, the final state of the reduced catalyst is very sensitive to reduction conditions [13].

More recently, Union Carbide has developed their own catalyst for ethylene polymerization [15]. The Carbide catalyst is made by supporting chromocene, $(\text{C}_5\text{H}_5)_2\text{Cr}$, on silica gel and is quite active. It is believed that the chromium is "anchored" to the support by reaction with a surface silanol group and subsequent loss of one cyclopentadienyl ligand [16]. Since the starting material is already in a low oxidation state, no reduction is necessary.

Unlike the Phillips catalyst, Union Carbide's catalyst produces polyethylene with saturated end groups. The difference has been attributed to the effect of the coordinated cyclopentadienyl ligand [17].

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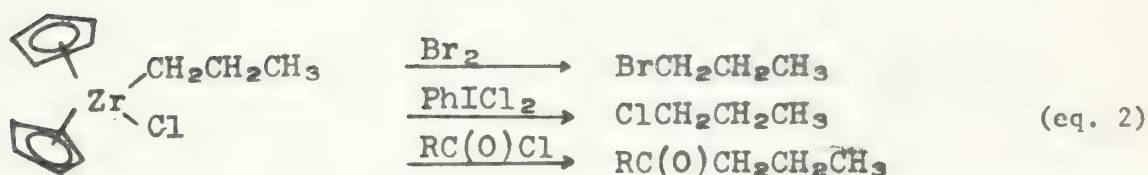
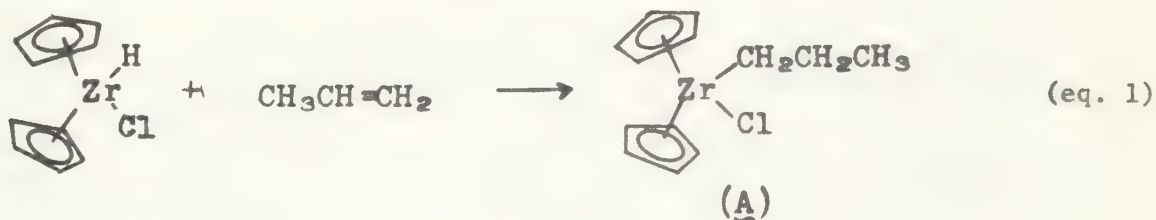
Peter Woyciesjes

April 8, 1980

Interest in developing transition metal hydrides as useful reagents in organic synthesis has led to the introduction of zirconium hydrides as attractive alternatives in standard synthetic procedures. The ease of handling and the versatility of zirconium hydrides in hydrometalation, transmetalation, and CO reduction reactions has contributed to their development in a number of areas.

I. Hydrozirconation [1-4]

The reaction of zirconium hydrides with unsaturated hydrocarbons under mild conditions gives high yields of stereospecific and regioselective organozirconium compounds (hydrozirconation) [1-3]. For example the reaction between 1-propylene and $\text{Cp}_2\text{Zr}(\text{H})\text{X}$ (eq. 1) results in the formation of $\text{Cp}_2\text{Zr}(\text{CH}_2\text{CH}_2\text{CH}_3)\text{X}$ (A). The ability of the organozirconium compounds, A, to react with a variety of electrophiles have made them valuable as synthetic intermediates [1] (eq. 2).



II. Reduction of CO [5-8]

It has been shown that organozirconium complexes cleanly undergo high yield CO insertions into the Zr-C bond to produce a stable zirconium acyl intermediate [5-6]. This intermediate can then be converted into a number of different organic products such as esters, aldehydes or carboxylic acids [5]. The main emphasis in this area has been placed in the development of zirconium (IV) complexes [7-8] which could act as possible Fischer-Tropsch catalysts. To date, they have not yet proved to be catalytic, but they have provided an opportunity for the examination of certain features of the reduction mechanism, especially the migratory insertion of CO into a transition metal hydride bond.

III. Transmetalation [9-11]

One shortcoming of organozirconium complexes has been that they have not yet been found to be effective reagents for routine formation of carbon-carbon bonds. In fact, the only useful direct carbon-carbon bond forming reaction observed thus far for $\text{Cp}_2\text{Zr}(\text{R})\text{Cl}$ alone is carbon monoxide insertion [5]. However, through extensive research it has been possible to overcome this limitation on the utility of organozirconium species. It was shown that η^1 -bound organic

ligands in $\text{Cp}_2\text{Zr(R)CL}$ could be transferred stereospecifically to other metal centers (transmetalation) [9-11]. Therefore, by selecting metal complexes whose use in carbon-carbon bond formation processes are well established, it is possible to take advantage of the ease and selectivity of hydrozirconation and of the carbon-carbon bond forming propensity of the other metallic element in an essentially 'one pot' reaction.

In summary organozirconium (IV) complexes have been shown to be extremely convenient precursors in a broad range of organic synthesis.

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Applications to Inorganic Chemistry of Magnetic Mossbauer Spectroscopy

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April 15, 1980

Introduction

The recoilless emission of γ -rays and their resonant reabsorption was discovered in 1958 by Rudolf Mössbauer [1]. This phenomenon, known as the Mössbauer effect, has proven to be of great use to chemists [2-5] as a probe of electronic environment around a single nucleus. The great importance of the effect is that it gives energy quanta of unparalleled precision. Because of this precision (ca. 1 in 10^{12}), minute changes in energy and resolution of hyperfine interactions, previously unobservable, can now be seen.

The three principal interactions are those of the electric monopole, known as the chemical shift, the magnetic dipole, and the electric quadrupole. The origin of the magnetic field which interacts with the magnetic moment of the nucleus may be intrinsic or extrinsic to the atom.

Theory

The application of an external magnetic field to a randomly-oriented powder can yield a great deal of new information about a compound. This approach was first applied by Collins [6] in his study of ferrocene.

When an external magnetic field is applied as a perturbation to the electric quadrupole interaction, i.e. $E_Q \gg E_M$ or when a "large" magnetic field is applied so that $E_M \gg E_Q$, the sign of the principal axis of the electric field gradient, V_{zz} , can be determined. For a substance such as iron, where only one of the nuclear states is quadrupolar, this information and the magnitude of the asymmetry parameter, η , may only be obtained when a magnetic field, internal or external, is seen by the nucleus, since the spectrum from the quadrupole interaction alone is symmetrical [7]. (A single crystal angular dependence study of the line intensities could also yield this information.)

The sign of an internal magnetic field can usually be obtained by the application of a large magnet if the magnetic anisotropy is small. If the resultant flux density has increased the sign is positive, whereas when there is antiparallel alignment of the internal and external magnetic fields the magnitude will decrease.

Time-dependent effects such as relaxation may also be studied by the application of both small and large magnetic fields [8-11].

Applications

Recently, the application of external magnetic fields to Mössbauer experiments on inorganic compounds has been expanding. Some examples include the studies of the $[(\eta^5\text{-C}_5\text{H}_5\text{FeS})_4]$ cluster [12], of bis(N,N-diakylthiocarbamato)-iron(III) halides [13], of dioxidized biferrocenylene [14], and of $\text{Fe}(2,9\text{-di-CH}_3\text{-phenanthroline})\text{SO}_4$ [15].

Hopefully, the application of magnetic fields to Mössbauer experiments will continue to increase as both the ease of technology and understanding of the phenomenon increases.

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Photochemistry of Transition Metal Carbonyl Clusters

Thomas R. Herrinton

April 24, 1980

Chemists have long known of the existence of metal carbonyl complexes; and the thermal reactivity, geometric structure, and electronic structure of these compounds have been (and still are) extensively studied. By contrast, the photochemistry of metal carbonyls has only been studied since the late 1950's [1]. Moreover, metal carbonyl cluster photochemistry has never received the attention the photochemistry of lower nuclearity complexes has, as only about two dozen papers have been published to date.

Early work [2] in this field dealt exclusively with the irradiation of $M_3(CO)_{12}$ compounds, where $M = Fe, Ru,$ and Os . In these studies photofragmentation generally occurred which, in the presence of appropriate ligands, lead to substituted monomeric and occasionally substituted dimeric species. However, some work indicated that $Fe_3(CO)_{12}$ and $Os_3(CO)_{12}$ complexes sometimes remained intact and formed substituted trimers upon irradiation. The focus of these studies was primarily synthetic in nature, with kinetic and mechanistic information rarely being examined.

Work [3,4] on the electronic structures and spectra of metal carbonyl clusters has contributed greatly to an understanding of their photochemistry. One paper [3] on these properties for $M_3(CO)_{12}$ complexes has shown that a metal bonding to metal anti-bonding ($\sigma \rightarrow \sigma^*$) transition is observed which is similar to those found for dimers. This absorption characteristically sharpens and blue-shifts upon cooling for dimers, trimers, and tetramers. An additional band in the spectrum is assigned to a metal anti-bonding to metal anti-bonding ($\sigma^* \rightarrow \sigma^*$) transition. The photochemistry of these compounds is explained in terms of the relative energies of these transitions and metal-metal bond strengths. Extensions to related trimeric and tetrameric species have also been made [3].

Later work has concentrated more on the photophysical aspects of the photochemistry of these clusters. In addition to further work on $M_3(CO)_{12}$ complexes [5,6,7], studies have been done using $Fe(CO)_5$ [7], $[(\eta^5-C_5H_5)Fe(CO)]_4$ [8], $Ru_3(CO)_9(PPh_3)_3$ [9], $H_3Re_3(CO)_{12}$ [10], $H_3Mn_3(CO)_{12}$ [10], capped $Co_3(CO)_9$ clusters [11], $Ir_4(CO)_{12}$ [12], $H_4Ru_4(CO)_{12}$ [13], and $H_4Os_4(CO)_{12}$ [14,15]. Products isolated include mono- and di-substituted monomers [5,6], unsubstituted and substituted dimers [10,11], and substitution products of the intact clusters [12-15]. Additionally, isomerization [9,13], reduction [13], and dehydrogenation [14,15] of olefins has also been observed. These reactions can be rationalized in terms of at least two competing primary photoprocesses: metal-metal bond cleavage and CO loss. Also, studies [7,8] show that bridging CO groups (but not bridging H's) can lend stability to a cluster during photolysis.

Further work in the photochemistry of metal carbonyl clusters is needed to clarify the mechanisms which have been proposed, to extend the list of clusters studied in order to verify the generalizations already made, and to investigate whether new chemistry will result from the irradiation of higher nuclearity clusters.

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Michael J. Desmond

June 24, 1980

The realization of the importance of multimetallic centers in catalysis has led to the study of complexes of binucleating ligands [1-3]. The recent observation of the reactions of ionic binuclear complexes with substrate molecules such as CO and H₂ should enhance study in the area [4]. A major limitation of all the charge neutral complexes of binucleating ligands reported to date has been their low solubility. Insolubility results in limitation to the use of only solid state techniques in the study of the complexes.

The synthesis of binuclear ligand complexes with appreciable solubility in non-polar or non-coordinating solvents allows extensive study of the solution properties and chemistry of the bimetallo-lomers. 4-tert-Butyl-bis-2,6-[N-(S-heptyl-dithiocarbamate)-formimidoyl]-phenol, based on a ligand system by McFadyen, Robson and Schaap [5], was synthesized to give complexes with the desired solubility and some potentially interesting chemistry. This bright yellow compound with its heptyl "wings" and tert-butyl "tail" is called Big Bird (abbr. BB) as a simplified name. Neutral complexes are usually produced from the metal acetate and an additional anionic bridging ligand. Complexes of the form M₂BBX have been synthesized from Cu(II) (X=⁻OEt, ⁻OMe, ⁻OH, N₃⁻, SCN⁻, I⁻, ⁻Sφ), Ni(II) (X=⁻OEt, ⁻OMe, ⁻OH, N₃⁻, I⁻), VO(IV) (X=⁻OEt, ⁻OMe), Zn(II) (X=⁻OEt, ⁻OH), Rh(II) (X=⁻OEt, ⁻OMe), Pd(II) (X=⁻OEt), and Hg(II) (X=⁻OEt). Mn(II) and Fe(II) do not form isolatable dimers, while Co(II) reacts in the presence of O₂ to produce Co(III)Co(II)BB(OEt)-(OAc) [6]. All of the complexes of the first-row transition metals have solubilities of approximately 10⁻¹M in aromatic and chlorinated hydrocarbon solvents. Second- and third-row transition metal complexes are an order of magnitude less soluble.

The Cu(II) and VO(IV) complexes are diamagnetic at room temperature with the exception of the iodo bridged copper complex ($\mu_{\text{eff}} < 0.20$). The diamagnetism indicates strongly interacting metal centers. All of the Ni(II) complexes are diamagnetic, and the mixed valence Co(III)-Co(II) complex contains a high spin Co(II) ($\mu_{\text{eff}} = 3.04$).

Electrochemical studies of the Cu(II) complexes in DMF showed similar properties to the binuclear complex of Gagne [7]. Two well isolated quasi-reversible one-electron reductions of the bis-Cu(II) complexes resulted. Some Ni(II) and VO(IV) complexes also exhibited quasi-reversible behavior.

The alkoxide bridged complexes are labile toward metal exchange reactions. Significant concentrations of mixed metal species slowly form from the homonuclear complexes in solution. Mixed VO(IV)-Ni(II) and Cu(II)-Ni(II) complexes exhibit the expected paramagnetic properties.

The Ni(II) complexes react readily with monodentate Lewis bases to form 2:1 base-to-acid adducts, which produces a mixed spin system ($\mu_{\text{eff}} = 2.00$). The presence of an averaged contact shifted NMR spectrum indicates fast exchange of the axial base on the NMR timescale at ambient temperatures.

Co(III)Co(II)BB(OEt)(OAc) reacts reversibly with dioxygen at low temperatures (liquid N₂) to form an end-bound adduct. The complex also slowly catalyzes the oxidation of 2,6-alkyldisubstituted phenols in the presence of coordinating base such as pyridine, at 30°C.

The many other potential reactions of Big Bird complexes warrant further study of this ligand and its compounds.

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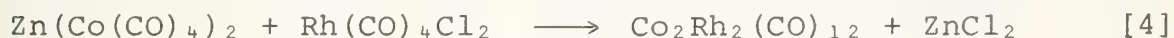
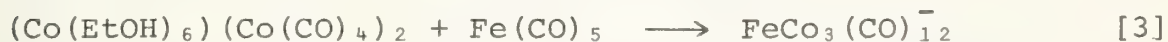
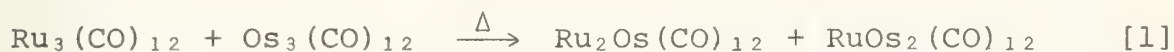
Final Seminar

Synthesis of Mixed Transition Metal Clusters of Osmium and Rhenium Via Metal Hydride Coupling Reactions

Greg Pearson

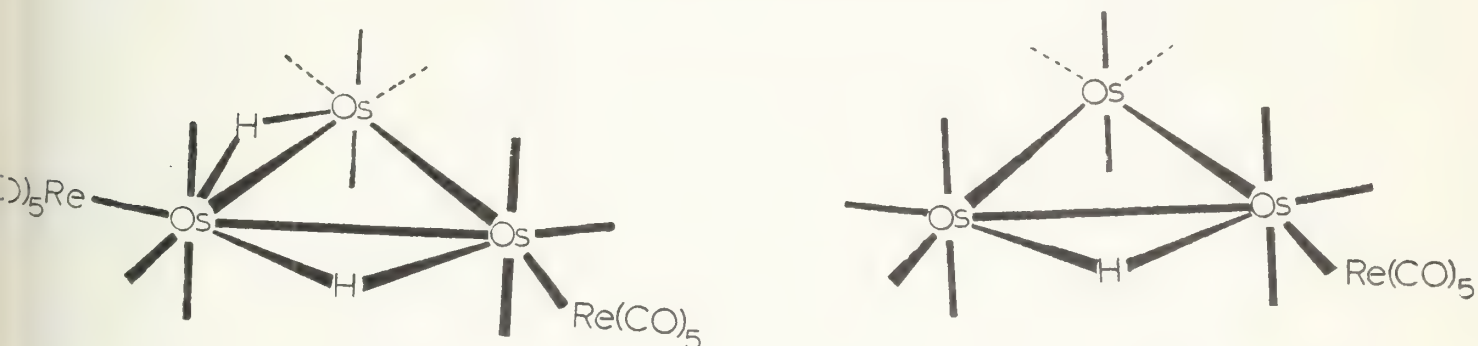
August 18, 1980

A few examples of the traditional methods for the production of mixed metal clusters are as follows:



These techniques have been used successfully to produce a large variety of mixed metal clusters. However, these methods frequently give complicated reaction mixtures that are difficult to work up.

The metal hydride coupling reaction [5], which has been used here to produce mixed metal clusters, is dependent upon the $\text{HRe}(\text{CO})_5$ unit initially serving as a two electron donor to the lightly stabilized clusters $\text{Os}_3(\text{CO})_{12-x}\text{S}_x$ ($\text{S} = \text{CH}_3\text{CN}$, C_6H_{14} ; $x = 1$ or 2). This ligating ability has been previously demonstrated by the production of $\text{MnRe}_2(\text{CO})_{14}\text{H}$ [6]. From this point, all that is necessary to achieve the final structures of $\text{HReOs}_3(\text{CO})_{16}$ and $\text{H}_2\text{Re}_2\text{Os}_3(\text{CO})_{20}$ is for an oxidative addition to take place. These two compounds are related by a third, lightly stabilized species, $\text{HReOs}_3(\text{CO})_{15}(\text{CH}_3\text{CN})$.



It has been found that the open molecular structure of this lightly stabilized species may be transformed to a closed structure either by heating in the presence of H_2 or by treating with $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ in the presence of H_2 . The product of this closure process is $\text{H}_5\text{ReOs}_3(\text{CO})_{12}$.

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Final Seminar

Synthesis and Reactions of
 π -Cyclopentadienylcarbonyliridiumdihydride and
 π -Cyclopentadienyldicarbonylrheniumdihydride

Paul C. Adair

August 19, 1980

CpIr(CO)H_2 was formed in high yield by the action of a zinc/ acetic acid/methanol reducing system [1] on the corresponding dibromide, CpIr(CO)Br_2 . This colorless, volatile oil is fairly air stable and is solution stable in non-donating solvents such as benzene or dichloromethane for several weeks at room temperature. In donating solvents such as acetone or THF or in hydrocarbon solvents at higher temperature, the solution darkens quickly (in acetone, degradation is essentially complete in three days). Three of the decomposition products have been identified as $\text{Cp}_3\text{Ir}_3(\text{CO})_3$, $\text{Cp}_4\text{Ir}_4(\text{CO})_3$, and $\text{Cp}_4\text{Ir}_4(\text{CO})_2$.

Results from this laboratory have indicated that trimethylamine oxide facilitates metal cluster formation from the compounds CpRh(CO)_2 [2] and CpIr(CO)_2 [3]. In the latter case the clusters $\text{Cp}_3\text{Ir}_3(\text{CO})_3$ and $\text{Cp}_4\text{Ir}_4(\text{CO})_3$ mentioned above were formed, albeit in lower yields than by the decomposition of CpIr(CO)H_2 . This reaction is thought to proceed by the oxidative decarbonylation of CpIr(CO)_2 to produce the unsaturated intermediate, CpIr(CO) , which could subsequently form metal-metal bonds by reaction with other solution species. The similarity of the products of the Me_3NO reaction to those of CpIr(CO)H_2 decomposition leads one to suspect that the intermediate in the latter reaction is also CpIr(CO) , which could be generated by the simple reductive elimination of hydrogen.

Under conditions under which it normally decomposes, CpIr(CO)H_2 is stable under moderate hydrogen pressure. The exchange of deuterium-labelled dihydride with hydrogen was studied by ^1H NMR in both tetrahydrofuran and decane, with exchange in THF being about four times faster than in non-donating decane.

A series of reactions were performed to trap the intermediate CpIr(CO) by decomposing the dihydride in the presence of added ligand. CpIr(CO)L (L = carbon monoxide, triphenylphosphine [4], dimethylphenylphosphine, or *t*-butylisonitrile) was formed in this way. For L = diphenylacetylene, a series of multi-iridium species were formed which are analogous to known compounds of bis(pentafluorophenyl)acetylene [5]. The reaction of CpIr(CO)H_2 with benzaldehyde yielded CpIr(CO)_2 and benzene.

In addition to providing a route to substituted mono-iridium species and higher iridium clusters, CpIr(CO)H_2 was used to incorporate iridium into mixed-metal clusters. $\text{Cp}_3\text{Rh}_2\text{Ir(CO)}_3$, $(\text{COD})\text{PtCp}_2\text{Ir}_2(\text{CO})_2$, and $\text{Cp}_2\text{RhIr(CO)}_3$ were prepared by the reaction of dihydride with $\text{Cp}_2\text{Rh}_2(\text{CO})_3$, $(\text{COD})\text{Pt(CH}_3)_2$, and CpRh(CO)_2 , respectively.

Two analogues of CpIr(CO)H_2 were made in order to compare reactivity to that of the dihydride. $\text{CpIr(CO)(CH}_3)_2$ was formed by

reacting methyllithium with $\text{CpIr}(\text{CO})\text{Br}_2$ and was found to be very thermally stable (decomp. 200°C). $\text{CpIrPPh}_3\text{H}_2$ was formed by the reduction of $\text{CpIrPPh}_3\text{Br}_2$ [4] and was found to decompose in refluxing toluene.

$\text{CpRe}(\text{CO})_2\text{H}_2$

The reduction of either lat- or diag- $\text{CpRe}(\text{CO})_2\text{Br}_2$ [6] resulted in the formation of the same isomer of $\text{CpRe}(\text{CO})_2\text{H}_2$. Comparison of carbonyl stretches in the infrared spectrum indicates that a diagonal configuration is adopted. Decomposition of $\text{CpRe}(\text{CO})_2\text{H}_2$ in xylene results in two isolable species, $\text{Cp}_2\text{Re}_2(\text{CO})_3$ and $\text{Cp}_3\text{Re}_3(\text{CO})_4$. The former complex contains a formal rhenium-rhenium triple bond and reacts with carbon monoxide under mild conditions to form the known $\text{Cp}_2\text{Re}_2(\text{CO})_5$ [7].

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Catalysis Using Supported Ruthenium Cluster Compounds

Virgil L. Payne

Final Seminar

September 18, 1980

A problem encountered in the attempt to understand supported metal catalysts is the preparation of a material having a large proportion of similar active sites. The use of aqueous solutions of metal salts often gives rise to a distribution of metal particle sizes and, consequently, a variety of active sites.

The suggestion that metal cluster compounds may serve as models for chemisorption on metal surfaces has led to their use as precursors for catalytically active species with well-defined structures. Previous research [1-3] using supported metal cluster carbonyl compounds suggests that under comparatively mild thermal conditions ($<200^{\circ}\text{C}$), CO may be reversibly dissociated from the cluster with no apparent loss of structural integrity.

The present research concentrates on the preparation, catalytic behavior and characterization of supported metal particles derived from the cluster compounds $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}_4\text{H}_4(\text{CO})_{12}$ and $\text{Ru}_6\text{C}(\text{CO})_{14}\text{C}_7\text{H}_8$. These clusters were dispersed in very low concentration on high surface area alumina and silica and low area titania in an effort to produce isolated triplets, quartets and sextets of ruthenium atoms.

Using the hydrogenolysis/dehydrogenation of n-butane as a diagnostic tool, it was observed that the catalytic behavior depends on the particular cluster as well as the pretreatment conditions and the support. While the Ru_3 - and Ru_4 -derived catalysts were similar with respect to selectivity towards the formation of methane, they differed greatly in comparison with the Ru_6 -derived catalysts, which produced almost twice as much methane under similar conditions.

There were no dramatic differences between the activities of the supported clusters, although catalysts derived from the traditional impregnation of supports with RuCl_3 were nearly twice as active as the cluster-derived catalysts. Silica-supported catalysts were generally more active than alumina- or titania-supported catalysts.

Physical characterization of the catalysts using hydrogen and carbon monoxide chemisorption revealed an uptake of less than 0.2 hydrogen atoms per ruthenium atom, indicative of a poorly dispersed catalyst. However, the samples exhibited an average CO uptake of one molecule per ruthenium atom. Since no large ruthenium particles could be observed using electron microscopy, this behavior could be attributed to metal-support interactions, as suggested by Bell [4] and Basset and coworkers [5,6].

In conclusion, the evidence gathered using the ruthenium cluster compounds as precursors for supported metal particles suggests that decarbonylation and activation of the compounds

gives rise to catalytically active species which interact strongly with the support, perhaps leading to oxidation of the metal. The observed product distributions suggest an increase in the extent of cracking of the butane molecule as the nuclearity of the initial cluster compound increases. This further suggests some retention of structure of the original cluster, even under severe catalytic conditions.

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Properties of Bimetallic Catalysts
Prepared from Alumina Supported Mixed Metal Carbonyls

Steve Hardwick Final Seminar September 18, 1980

Supported bimetallic catalysts represent an important class of commercial catalysts [1,2]. Despite intensive study, a great deal remains to be learned about these systems. One difficulty associated with the characterization of supported metal catalysts is the variability of sites. Classically prepared bimetallic catalysts usually contain metal sites of varying size and stoichiometry. It has been suggested that decarbonylation of mixed metal carbonyl clusters could be used to prepare metal crystallites of well defined size and stoichiometry [3].

Systems involving cobalt-rhodium mixed metal carbonyls have been the most extensively studied [3-6]. Aggregation of the clusters and cobalt enrichment of the surface have been found to complicate the preparation of well defined surface species in this system [4]. Nonetheless, observations of intriguing catalytic behavior have continued to make these mixed metal complexes [3,5,6] and others [7] attractive for study. The goal of the present study was to prepare highly dispersed metal particles using mixed metal carbonyl clusters as precursors. Chemisorption, catalytic activity and reactive thermal desorption (RTD) were used to characterize these catalysts.

Hydrogenation of ethene was investigated over a series of alumina supported iron-ruthenium mixed metal carbonyls. The observed order of activity was:



$\text{Ru}_3(\text{CO})_{12}$ was approximately two orders of magnitude more active than $\text{Fe}_3(\text{CO})_{12}$. The catalytic activities of the mixed metal carbonyls were approximately what one would expect from additive behavior of $\text{Ru}_3(\text{CO})_{12}$ and $\text{Fe}_3(\text{CO})_{12}$.

A series of complexes of the general formula $\text{CpMOS}_3(\text{CO})_{12}\text{H}$, where M = Mo or W, supported on alumina were also investigated [8]. During activation in hydrogen most of the carbonyl ligands were hydrogenated to form methane. RTD of alumina supported $\text{Os}_3(\text{CO})_{12}$ and $\text{CpMOS}_3(\text{CO})_{12}\text{H}$ complexes showed similar decarbonylation behavior for all three complexes. CO/Os ratios of 1-1.2 indicated that the resulting metal particles were highly dispersed. Studies employing catalytic methanation of carbon monoxide showed that all three clusters had similar activity, selectivity and activation energies, indicating that osmium was solely responsible for the catalytic behavior of these supported metal catalysts.

Hydrogenolysis was used as a probe to study the nature of alumina supported catalysts of the general formula $\text{Cp}_n\text{W}_n\text{Ir}_{4-n}(\text{CO})_{12-n}$, where $n = 0-2$. Differences in activity selectivity and activation energy for n-butane hydrogenolysis were observed over this series of catalysts. These catalysts were highly dispersed, as shown by hydrogen and carbon monoxide chemisorption. Activation in hydrogen once again resulted in hydrogenation of most of the carbonyl ligands. Unlike the supported $\text{CpMoS}_3(\text{CO})_{12}\text{H}$ complexes, the tungsten-iridium mixed metal clusters gave RTD curves characteristic of the individual clusters.

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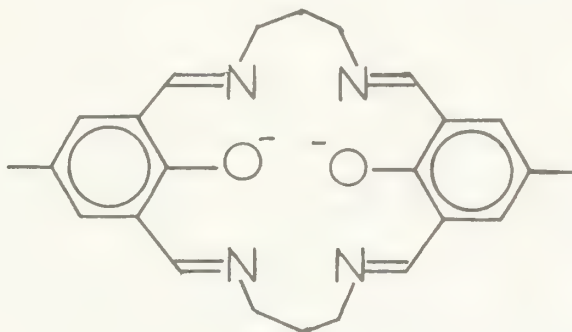
Magnetic Exchange Interactions and Mixed Valence Chemistry in Binuclear Transition Metal Complexes

Susan L. Lambert

September 16, 1980

Coupled metal centers play a very important role in both natural [1] and synthetic [2] catalysts. For this reason there is a growing interest in binuclear transition metal complexes [3,4]. Characterization of the magnetic exchange interactions for several series of related binuclear compounds have, in the past, yielded insight into factors which affect the interaction between two metal ions [5-7]. The results of a study of three related series of binuclear compounds, where the binucleating ligand is held constant and the metal ion is varied, are reported in this seminar.

A series of five-coordinate complexes of the binucleating ligand L, illustrated below, were synthesized by the method of



Pilkington and Robson [8]. Variable temperature magnetic susceptibility data were obtained for the series LM_2X_2 where $M(II)$ is $Mn(II)$, $Fe(II)$, $Co(II)$, $Ni(II)$ and $Cu(II)$. The magnetic exchange interaction observed for each complex was assessed with the isotropic spin Hamiltonian, $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$. It was found that the net antiferromagnetic interaction decreases monotonically in the series LM_2X_2 where M is copper ($J = -294 \text{ cm}^{-1}$), nickel ($J = -27. \text{ cm}^{-1}$), cobalt ($J = -9.3 \text{ cm}^{-1}$), and iron ($J = -4.2 \text{ cm}^{-1}$), to finally become a net ferromagnetic exchange interaction in the manganese complex ($J = +0.20 \text{ cm}^{-1}$). The variation in the J -value across this series is attributed to an increasing number of unpaired electrons and also to an increasing metal to ligand-plane distance in going from copper to manganese.

The response of the magnetic exchange interaction to changes in the metal ion coordination geometry was also investigated with a series of six-coordinate complexes of the ligand L. The complexes studied are $[LNi_2(py)_4](BF_4)_2$, $[LCo_2(py)_4](BF_4)_2$, $[LFe_2(py)_4](BF_4)_2$, $[LFe_2(MeIm)_4](BF_4)_2$, $[LFe_2(Im)_4](BF_4)_2$ and $[LFe_2(MeNic)_4](BF_4)_2$ where py is pyridine, $MeIm$ is 1-methylimidazole, Im is imidazole and $MeNic$ is the methyl ester of isonicotinic acid. The electronic spectra of these complexes are indicative of six-coordinate geometry. The results of the x-ray crystal structure of $[LFe_2(Im)_4](BF_4)_2$ show that the $Fe(II)$ coordination geometry is six-coordinate and that the $Fe(II)$ is located in the

plane of the macrocyclic ligand. With the metal ion located in the plane of the ligand one of the variable factors, i.e. metal to ligand-plane distance, in the five-coordinate case is eliminated. When the axial base is pyridine the ordering found for the antiferromagnetic exchange interaction is $\text{Ni(II)} > \text{Fe(II)} > \text{Co(II)}$. In the series of iron complexes the exchange interaction is observed to become less antiferromagnetic as the base strength of the axial ligand is increased. This observation leads us to the conclusion that the magnetic exchange interaction is responsive to changes in the ligand field strength. In the six-coordinate complexes, forcing the metal ion to lie in the ligand plane should increase the orbital overlap between the metal based orbitals and the orbitals on the bridging oxygen. This would cause the antiferromagnetic exchange to increase. On the other hand, the change from five-coordinate to six-coordinate geometry will result in a stronger ligand field about the metal ions. This leads to an enhanced difference in energies between metal based and ligand orbitals, which would decrease the antiferromagnetic exchange. From the data it appears that these two effects cancel.

A series of heterobinuclear complexes was also characterized via variable temperature magnetic susceptibility measurements. A trend in the magnetic exchange interaction analogous to that found in the homobinuclear, five-coordinate complexes was observed. For the complexes $\text{LCuM}'\text{Cl}_2$ the largest antiferromagnetic exchange is observed for $\text{M}' = \text{nickel}$ where $J = -125 \text{ cm}^{-1}$. J is observed to decrease monotonically for the series $\text{M}' = \text{Co(II)}$ ($J = -81. \text{ cm}^{-1}$), Fe(II) ($J = -75. \text{ cm}^{-1}$), and Mn(II) ($J = -30. \text{ cm}^{-1}$). This is the first reported series of heterobinuclear complexes with an entire analogous homobinuclear series available for comparison. Analysis of the orbital superexchange pathways indicated the presence of relatively fewer ferromagnetic contributions for $\text{LCuM}'\text{Cl}_2$ compared to $\text{LM}_2'\text{Cl}_2$.

Oxidation of the six-coordinate iron and cobalt species, $[\text{LM}_2(\text{B})_4](\text{BF}_4)_2$, where B is a nitrogenous base, to produce mixed valence compounds was also studied. Chemical oxidation of $[\text{LCo}_2(\text{Im})_4](\text{BF}_4)_2$ produced Co(II)-Co(III) dimers in which the cobalt (III) was, without exception, low spin and therefore diamagnetic. Also studied was the reaction of the six-coordinate cobalt compounds with oxygen. A sample of $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$ was obtained by oxidation of $[\text{LFe}_2(\text{Im})_4](\text{BF}_4)_2$ with AgBF_4 . The magnetic susceptibility data indicate the complex contains a high spin Fe(II) and a low spin Fe(III) with a small antiferromagnetic exchange interaction occurring between them.

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New Group VI - Group VIII Mixed-Metal Clusters

Daniel S. Foose

Final Seminar

September 15, 1980

Investigations of heteronuclear cluster complexes for use as precursors for the preparation of bimetallic and multimetallic heterogeneous catalysts [1,2,3], as homogeneous catalysts and as models which might serve to bridge the gap between the fields of homogeneous and heterogeneous catalysis have been hampered by the relative lack of availability of these compounds. [4] A real need exists for the development of general, systematic and efficient routes for their preparation. A relatively unexplored and potentially important approach to this problem involves the use of coordinatively unsaturated species. [5,6]

The coupling of the metal hydrido complex $\text{HW}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ with the "lightly stabilized" derivative $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ under mild conditions yielded an intermediate cluster complex $(\mu_2\text{-H})\text{WOs}_3(\text{CO})_{13}(\text{NCCH}_3)(\eta^5\text{-C}_5\text{H}_5)$. This complex, when heated with excess $\text{HW}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ under refluxing toluene conditions, produced the more condensed clusters $(\mu_2\text{-H})\text{WOs}_3(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)$ and $(\mu_2\text{-H})_3\text{WOs}_3(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$. It was also observed that $(\mu_2\text{-H})_3\text{WOs}_3(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$ could be prepared directly from $(\mu_2\text{-H})\text{WOs}_3(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)$ by reaction with hydrogen in refluxing toluene. $(\mu_2\text{-H})\text{MoOs}_3(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)$, $(\mu_2\text{-H})_3\text{MoOs}_3(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$, $(\mu_2\text{-H})\text{WRu}_3(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)$ and $(\mu_2\text{-H})\text{-MoRu}_3(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)$ were prepared by analogous reactions. Formulation of these complexes was on the basis of their NMR, infrared and mass spectra. The molecular configurations of $(\mu_2\text{-H})\text{WOs}_3(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)$ and $(\mu_2\text{-H})_3\text{WOs}_3(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$ were established by single crystal x-ray diffraction studies. [7]

$\text{WIr}_3(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$ and the previously reported $\text{WCo}_3(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$ and $\text{MoCo}_3(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$ [8] were also prepared by means of the metal hydride coupling reaction. A more logical approach for the preparation of cluster complexes containing both tungsten and iridium involved the reaction of the carbonylmetalate $\text{Na}[\text{W}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ with the metal halide complex $\text{IrCl}(\text{CO})_2(\text{p-toluidine})$. This reaction resulted in the formation of both $\text{W}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)_2$ (major product) and $\text{WIr}_3(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$ under relatively mild conditions. The combination of $\text{HW}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ with $\text{IrCl}(\text{CO})_2(\text{p-toluidine})$ over a period of twelve hours also resulted in the formation of these clusters. A small amount of acid-washed granular zinc or triethylamine added to the latter reaction mixture resulted in a significant decrease in reaction time. When the reaction was carried out with acid-washed granular zinc and warmed under a carbon monoxide atmosphere, $\text{WIr}_3(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$ resulted as the major product. When $\text{W}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)_2$ was treated under similar conditions no $\text{WIr}_3(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$ was produced. However, treatment of $\text{W}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)_2$ with carbon monoxide under considerably harsher thermal conditions resulted in conversion to the more stable $\text{WIr}_3(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$ and $\text{Ir}_4(\text{CO})_{12}$. A mechanism which involves metal-metal triple bonded intermediates for the formation and conversion of the clusters is suggested. $\text{Mo}_2\text{Ir}_2(\text{CO})_{10}(\eta^5\text{-C}_5\text{H}_5)_2$ and $\text{MoIr}_3(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)$ are readily prepared by the analogous reactions with $\text{Na}[\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$.

($\eta^5\text{-C}_5\text{H}_5$) and $\text{HMo(CO)}_3(\eta^5\text{-C}_5\text{H}_5)$. The new clusters were characterized by their NMR and infrared spectra. The molecular configurations of the tungsten-iridium clusters were determined by single crystal x-ray diffractometry.

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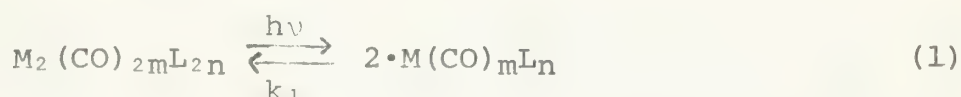
Kinetics and Mechanisms of Metal Carbonyl Radical Reactions

Richard Wegman

Final Seminar

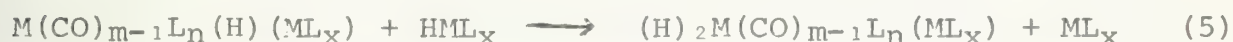
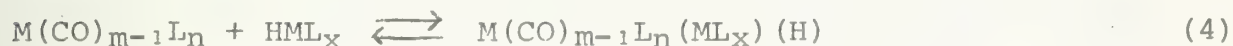
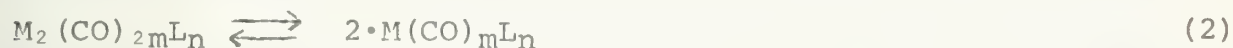
September 24, 1980

Dinuclear metal carbonyl compounds, $M_2(CO)_{2m}L_{2n}$, generally possess an intense absorption band ($\epsilon = 10^4 M^{-1}cm^{-1}$) in the range from about 310 to 500 nm. This absorption corresponds to a $\sigma \rightarrow \sigma^*$ transition of an electron in the metal-metal bond [1]. Irradiation into this absorption results in formation of the $\cdot M(CO)_mL_n$ radicals with high quantum efficiencies [2]:



In CO-saturated solutions recombination of the $\cdot M(CO)_mL_n$ radicals occurs with bimolecular rate constants, k_1 , on the order of 10^9 - $10^8 M^{-1}s^{-1}$. Flash photolysis of $M_2(CO)_{2m}L_{2n}$ in CO-free hexane solutions results in formation of a long-lived (400 ms) intermediate(s) [3,4]. Presumably, the intermediate(s) is an unsaturated dinuclear metal carbonyl compound resulting from loss of CO from $\cdot M(CO)_mL_n$ radicals followed by subsequent recombination of the $M(CO)_{m-1}L_n$ species with $\cdot M(CO)_mL_n$ or $M(CO)_{m-1}L_n$ radicals.

Initial formation of $\cdot M(CO)_mL_n$ radicals followed by loss of CO and subsequent oxidative addition of a metal hydride, HML_X , may represent a general mechanism for metal hydride reactions:



This mechanism is postulated to account for the reaction of $M_2(CO)_{2m}L_{2n}$ with $HSnR_3$, $HMn(CO)_5$ and $HMo(CO)_3(\eta^5-C_5H_5)$ and the thermal and photochemical decomposition reactions of $HCo(CO)_4$ [5].

The reaction of $HCo(CO)_3L$ with L ($L = P(n-Bu)_3$) results in formation of $HCo(CO)_2L_2$. An induction period, typically 10-50 seconds, is followed by rapid conversion ($t_{1/2} = 15$ -20 seconds) of $HCo(CO)_3L$ into $HCo(CO)_2L_2$. A free radical chain mechanism, analogous to the mechanism suggested for the substitution reactions of $HM(CO)_5$ ($M = Re, Mn$) [6] and $HM(CO)_3(\eta^5-C_5H_5)$ ($M = Mo, W$) [7], is postulated. In those cases where reactions of metal carbonyl hydrides have been studied in detail, free radical processes are indicated. Thus, free radicals may play an important role in many of the reactions involving cobalt carbonyl hydrides.

The reaction of $\text{HMo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ with HSnR_3 results in formation of $\text{Bu}_3\text{SnMo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$. The rate increases with increasing HSnBu_3 concentration. Interestingly, the reaction is not inhibited by added CO. The following mechanism accounts for the observations:



A is a reactive intermediate. The detailed nature of step (7) is not known. At this juncture an $\eta^5 \leftrightarrow \eta^1$ equilibrium involving the C_5H_5 ligand seems the most reasonable process leading to the intermediate A [8].

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Kinetics of Reaction of $\text{Co}_2(\text{CO})_8$ with Phosphines

Nancy P. Forbus

Final Seminar

September 25, 1980

Interest in $\text{Co}_2(\text{CO})_8$ arises from the fact that it is itself a catalyst [1], or the precursor for a catalyst [2] in several reactions, most notably the oxo process in which olefins are hydroformylated. $\text{Co}_2(\text{CO})_8$ is one of the more reactive of the simple binary carbonyls of transition metals. For example, reaction of $\text{Co}_2(\text{CO})_8$ with PPh_3 is complete in less than 10 seconds at 25°C [3]. By contrast, reaction of $\text{Mn}_2(\text{CO})_{10}$ with PPh_3 requires approximately 16 hours at 120°C to go to completion [4]. In an effort to understand this reactivity of $\text{Co}_2(\text{CO})_8$, kinetic studies have been carried out on reactions of $\text{Co}_2(\text{CO})_8$ with various phosphorus bases.

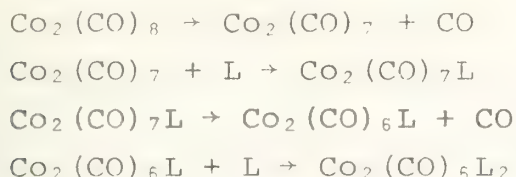
Basicity and steric requirement are two characteristics of phosphines which may affect the course of the reaction with $\text{Co}_2(\text{CO})_8$. The cone angle as defined by Tolman [5] has been used as a measure of the relative steric effect. As a means of comparing relative basicity, the A_1 carbonyl stretching mode of phosphine substituted $\text{Ni}(\text{CO})_3\text{L}$ has been used as the criterium.

The tri-alkyl phosphines, $\text{P}(\text{n-Bu})_3$, $\text{P}(\text{i-Pr})_3$ and $\text{P}(\text{t-Bu})_3$, have very similar basicities but widely varying cone angles. These were used to determine the effect of steric requirement on the course of reaction. To determine effect of relative basicity, reaction of $\text{P}(\text{n-Bu})_3$ and $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ with $\text{Co}_2(\text{CO})_8$ was compared. These two bases have the same cone angles, but the presence of the strongly electron-withdrawing CN-groups in $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ greatly reduces the basicity of this phosphine relative to that of $\text{P}(\text{n-Bu})_3$.

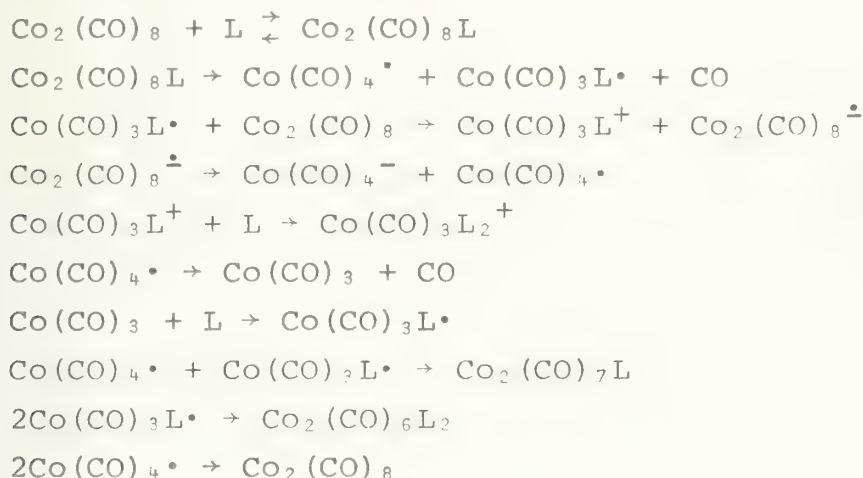
Both the rate of reaction and the products formed were found to be quite sensitive to the nature of the phosphine. Rates of reaction ranged from a half-life of 70 msec. for reaction with $\text{P}(\text{n-Bu})_3$ [6] to a half-life of about 45 seconds for reaction with $\text{P}(\text{t-Bu})_3$ and $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$. The only product formed in the reaction with $\text{P}(\text{n-Bu})_3$ is the ionic compound, $\text{Co}(\text{CO})_3\text{L}_2^+\text{Co}(\text{CO})_4^-$. The reaction with $\text{P}(\text{t-Bu})_3$ or $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ gives a mixture of $\text{Co}_2(\text{CO})_7\text{L}$ and $\text{Co}_2(\text{CO})_6\text{L}_2$ as product. Intermediate between these two extremes is the reaction of $\text{P}(\text{i-Pr})_3$ with a half-life of about 15 seconds. Products of the reaction with $\text{P}(\text{i-Pr})_3$ are a mixture of the ionic compound, $\text{Co}(\text{CO})_3\text{L}_2^+\text{Co}(\text{CO})_4^-$, and the disubstituted dinuclear compound, $\text{Co}_2(\text{CO})_6\text{L}_2$.

To determine possible intermediacy of monosubstituted dinuclear species in these reactions, the compounds $\text{Co}_2(\text{CO})_7\text{L}$ [$\text{L} = \text{P}(\text{n-Bu})_3$, $\text{P}(\text{i-Pr})_3$ and $\text{P}(\text{t-Bu})_3$] were prepared photochemically and their reaction with excess base was studied. The reaction with $\text{Co}_2(\text{CO})_7\text{P}(\text{n-Bu})_3$ and $\text{Co}_2(\text{CO})_7\text{P}(\text{i-Pr})_3$ with $\text{P}(\text{n-Bu})_3$ and $\text{P}(\text{i-Pr})_3$, respectively, was found to be slow relative to the corresponding reaction of $\text{Co}_2(\text{CO})_8$ with these bases. Reaction of $\text{Co}_2(\text{CO})_7\text{P}(\text{t-Bu})_3$ with $\text{P}(\text{t-Bu})_3$ occurs at a rate that is rapid relative to the reaction of $\text{Co}_2(\text{CO})_8$ with $\text{P}(\text{t-Bu})_3$.

These results suggest two competitive mechanisms for reaction of $\text{Co}_2(\text{CO})_8$ with phosphines. The simplest mechanism involves a rate-determining CO dissociation from $\text{Co}_2(\text{CO})_8$ as shown below:



A much more complex mechanism appears to be operating in reactions where ionic products are obtained. In this case, a radical chain process involving an outer-sphere electron transfer is proposed. This mechanism is:



A computer modeling study using the program described by Chesick and Stabler [7] has been performed on this radical mechanism. Reaction of $\text{Co}_2(\text{CO})_8$ with $\text{P}(\text{n-Bu})_3$ at 25°C and at -15°C was modeled. Using reasonable values for the rate constants, excellent agreement with experiment is obtained. Both rate of reaction and order in base is fit very well using the radical chain mechanism. In addition, the model accounts for variation in order in $\text{Co}_2(\text{CO})_8$ as a function of temperature.

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Selective Chemical Conversions Using Sheet Silicate Intercalates

Michael F. Moore

September 30, 1980

Introduction

Details of the structure of clay minerals, together with their identification by x-ray diffraction, have been discussed by Grim [1]. As the name suggests, the layer silicates are essentially made up of layers formed by condensation of sheets of linked $\text{Si}(\text{O}, \text{OH})_4$ tetrahedra with those of linked $\text{M}_{2-3}(\text{OH})_6$ octahedra, where M is either a divalent or trivalent cation. Condensation in a 1:1 proportion gives rise to the two-sheet minerals of which kaolinite is, perhaps, the best-known example. Similarly, the three-sheet clays are formed by a 2:1 condensation, the octahedral layer being sandwiched between two sheets of inward-pointing tetrahedra. Examples of these latter clays include the montmorillonites and vermiculites.

There exist in the type 2:1 minerals broad capabilities for isomorphous replacement, that is, for substitution of Si^{4+} and/or $\text{M}^{2+}/^{3+}$ for cations of similar size but different valency. As a result of this isomorphous substitution the structure of many phyllosilicates is negatively charged. This positive charge deficiency is compensated for, in the most part, by the sorption of extraneous cations, which may or may not be exchangeable.

Structural Considerations

The current belief that, the reluctance of metal ions to function as catalysts in the interlayer environment is related in large part to their lack of solution-like character under normal conditions, has gained wide acceptance. The absence of solution-like properties when the exchange cations are solvated by a monolayer of water is exemplified by the epr spectrum of oriented $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ -hectorite samples [2]. Under these conditions the planar complex is restricted to an orientation in which the plane of the ion is parallel to the silicate layers. Copper(II) ions hydrated by two or three molecular layers of water also adopt highly restricted orientations with the symmetry axis of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ion at an angle near 45° or 90° , respectively, to the silicate layers. Hydration then, by one to three molecular layers of water leads to a rather rigid metal ion-solvent structure of low mobility in which significant metal ion catalytic activity is not observed due to the unfavorable diffusion of reactant molecules into the interlayer region.

Rapid molecular tumbling and appreciable solution-like character can be achieved however when $\text{Cu}(\text{II})$ -hectorite is fully swelled by multilayers of water. Epr line width measurements of $\text{Mn}(\text{II})$ -hectorite suggest that the precollision lifetime of the ion is only ca. 30% longer in the interlayer region than that observed

in dilute bulk solution [3]. It has been proposed therefore that the conditions for observing a metal-ion catalyzed reaction in the interlayer space should be optimized when the distance between the silicate sheets exceeds the dimensions of the inner coordination sphere of the exchange ion complex.

Selective Chemical Conversions

The intercalation of a wide range of organic molecules into various sheet silicates has been reviewed by Theng [4]. It has been known for some time that clay minerals are capable of functioning as catalysts for a number of organic reactions [4,5].

One particularly efficient reaction is the thermally induced conversion to aniline of the 4,4'-diaminostilbene intercalate of a sodium-exchanged montmorillonite. This reaction which proceeds rapidly at ca. 270°C yields aniline (close to 45% of the parent diamine) as the sole gaseous product [6].

Both trans-stilbene and indene (each introduced separately) from the vapor into dehydrated Cu(II)-montmorillonite) yield oligomeric products in which no loss of hydrogen atoms has occurred [7].

Cu(II)-montmorillonite is also a very good catalyst for the production of 1-methyl-1,3,3-triphenylindane from 1,1-diphenylethylene at low temperature [8].

Conversion of 1-hexene, 1-heptene, or 1-octene to the corresponding bis-*sec*-alkyl ethers is readily accomplished by reflux of the appropriate alkene in a hexane solution with one of a range of cation-exchanged montmorillonites [9]. It is interesting that the synthesis of these ethers is so facile in clay and yet cannot be practicably prepared by any other method.

Dirhodium(II) ions, Rh_2^{4+} , have been bonded to the planar surfaces of hectorite by an exchange reaction between the proton exchange form of the mineral and Rh_2^{4+} in methanol solution under oxygen-free conditions. Though Rh_2^{4+} is inactive as an olefin hydrogenation catalyst in homogeneous solution, the intercalated ion readily catalyzes the reduction of 1-hexene in methanol at 25°C and ordinary H_2 pressure [10]. Reaction of Rh_2^{4+} -hectorite and triphenylphosphine (PPh_3) affords a mineral-bonded $\text{Rh}(\text{PPh}_3)_3^+$ complex which is more efficient than Rh_2^{4+} -hectorite as a catalyst.

Reaction of H^+ -, Na^+ -, or $\text{N}(\text{CH}_3)_4^+$ -hectorite with Rh_2^{4+} in methanol in the presence of air and catalytic amounts of HF affords a Rh(III)-hectorite. This catalyst is highly specific for the reduction of acetylenes. In the absence of PPh_3 , Rh(III)-hectorite is reduced to Rh(O)-hectorite which is a catalyst for the hydrogenation of acetylenes, olefins, and aromatic molecules.

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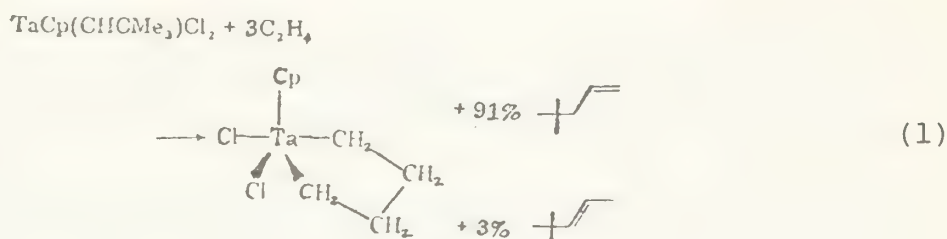
Review articles

Tantalacyclopentane Complexes: Their Synthesis, Characterization, and Use as Olefin Dimerization Catalysts

Gail Rattinger

October 16, 1980

Metallacyclopentane complexes have been found to catalyze the dimerization of high energy olefins such as norbornadiene and methylenecyclopropene [1-3]. In addition, it has recently been found that nickelacyclopentane complexes catalyze the dimerization of ethylene to cyclobutane and butenes [4]. In 1977 Schrock and co-workers found that olefins reacted with $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\text{CHCMe}_3)\text{Cl}_2$ to give tantalacyclopentane complexes [5]. For example, the reaction with ethylene yields:



It was then found that these tantalacyclopentane complexes were able to catalytically and selectively dimerize monosubstituted α -olefins (RCH=CH_2) [6-9].

Dichloromonocyclopentadienyl tantalum(V) cyclopentane complexes can be prepared by reacting dichloromonocyclopentadienyl neopentylidene tantalum(III) complexes with olefins [10]. The dichloromonocyclopentadienyl neopentylidene tantalum(III) complexes are prepared by reacting penachlorotantalum(V) with dineopentyl zinc [11,12].

Many dichloromonopentamethylcyclopentadienyl tantalum(V) cyclopentane complexes are synthesized from dichloromonopentamethylcyclopentadienyl (α -olefin) tantalum(III) complexes and a dialkylzinc reagent [10]. All compounds are water and air sensitive so the reactions are performed under a nitrogen atmosphere. The tantalacyclopentane complexes were characterized by ^1H and ^{13}C NMR and were found to be trans- β,β' -disubstituted tantalacyclopentane complexes [5,9,10]. The existence of α,β' -disubstituted tantalacyclopentane complexes was postulated although none were observed by NMR techniques [5,9].

Schrock has recently found that both the monocyclopentadienyl and monopentamethylcyclopentadienyl tantalacyclopentane complexes are active catalysts for monosubstituted α -olefin dimerization [6-9]. In the presence of excess olefin an equilibrium between the tantalum(V) cyclopentane complex and the tantalum(III) olefin complex is established. Decomposition of the tantalacyclopentane complex results in formation of an olefin dimer. The turnover rate for these olefin dimerizations is approximately one per hour at 30°C .

The dimerization mechanism was probed by using deuterium labelling studies. Schrock has proposed that the mechanism consists of four steps: 1) β -H elimination from the tantalacyclopentane complex to form a butenyl hydride, 2) ring contraction to form a tantalacyclobutane intermediate, 3) allyl hydride formation and 4) reductive elimination to give the observed olefin dimer [8,9,13]. Also Schrock proposes that β -H elimination is facile for these tantalacyclopentane complexes, which is in contrast to the platinum and titanium cyclopentane decompositions studied by Whitesides [14,15]. Schrock proposes that the differences in crystal structures of the platinum and tantalum cyclopentane systems may be related to the ease of β -H elimination [9,16,17].

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Applications of Magic Angle NMR

Dorothy Hamilton

October 23, 1980

Development

In contrast to spectra of solutions, conventional NMR spectra of solids characteristically consist of broad, poorly resolved lines, from which little information can be obtained. The major source of this broadening is dipole-dipole interactions between nuclei in the sample. These interactions are averaged to zero in solution due to rapid molecular motion, but are often on the order of 10^3 - 10^4 Hz in solids. Since the dipolar contribution contains a $(1-3\cos^2 \theta)$ angular dependence, a value of $\theta = 54.7^\circ$ will eliminate dipolar broadening. Therefore, by spinning the sample at this "magic angle" at a rotational speed which is large compared to the magnitude of the interaction (≥ 10 kHz), the dipolar broadening (and fortuitously, broadening from chemical shift anisotropy) is removed [1-5].

Magic angle spinning was first used by Lowe [6] and by Andrew, et. al. [7] in 1959. In these studies relatively small dipole-dipole interactions were present. However, when these interactions are large (which is common), the necessary spinning rates are not attainable practically.

Schaefer and Stejskal [8,9] showed that systems containing rare spins (e.g. ^{13}C) in the presence of abundant spins (e.g. ^1H) could be studied. By a combination of techniques--cross-polarization from abundant to rare spins to improve signal-to-noise ratio, decoupling of the abundant spins to repress heteronuclear dipolar interactions, and magic angle spinning at 2-4 kHz to remove remaining dipolar broadening and chemical shift anisotropy--high resolution NMR spectra of many solids could be obtained.

Applications

There have been many recent applications of ^{13}C NMR for characterization of solids. Schaefer and Stejskal obtained high-resolution spectra of polysulfone, wood, and ivory in the solid state, and compared to spectra obtained in solution [8]. They also studied the spectra of several polymers to gain information about motions of the polymers in the solid state [9]. Fyfe, et. al. looked at insoluble aromatic polyesters, and concluded that the polymer chain was highly rigid [10]. Opella, et. al. suggested that selection of nonprotonated carbon resonances could be used to study complex molecules, and applied this to biologically important molecules [11,12]. Comparison of the conformers cellulose I and II by Attalla, et. al. led them to conclude that these structures are best represented as repeating units consisting of a glucose dimer [13].

Nuclei other than ^{13}C have also been studied. ^{31}P has been used by Waugh and co-workers to characterize solid calcium phosphates [14]. Lippmaa, et. al. used ^{29}Si to study the structures of silicates and aluminosilicates [15].

Magic angle spinning has also been used to show that chemical exchange can occur in the solid state. Fyfe, et. al. have presented evidence that in naphthazarin, proton exchange occurs at room temperature [16]. A study of $\text{Ru}_3(\text{CO})_2(\text{COT})_2$ showed that rapid chemical exchange is occurring in the solid state, similar to that known to occur in solution [17].

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Platinum-Rhenium Reforming Catalysts

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October 29, 1980

Introduction

Catalytic reforming, the treatment of a hydrocarbon fraction to improve its octane number, has become one of the largest volume catalytic processes in industry due to the increasing environmental concern about the pollution caused by motor vehicles. In 1967, Standard Oil of California (Chevron) [1] introduced a bimetallic platinum-rhenium reforming catalyst. This bimetallic catalyst yields major improvements over conventional platinum reforming catalysts, in particular low yield decline with temperature and better product distribution selectivity [2].

During the past 10 years, many laboratory investigations were directed toward understanding the nature of rhenium on the bimetallic catalysts. Major efforts were made to elucidate the oxidation state of rhenium and its interaction with platinum under reforming conditions.

Oxidation State of Re on Re/Al₂O₃

Johnson and LeRoy [3] have presented evidence from hydrogen consumption and fluoboric acid leaching experiments that alumina supported rhenium is reduced from Re⁷⁺ to Re⁴⁺ after reduction at 482° or 625°C. Alternatively, Webb [4] claimed the metallic rhenium state (Re⁰) is reached after reducing the catalyst under hydrogen at 400°C for 19 hours. Temperature-programmed reduction studies (TPR) carried out by three separate research groups showed complete reduction of rhenium is attainable at 550°C [5,6,7].

Oxidation State of Re on Pt-Re/Al₂O₃

Hydrogen consumption and fluoboric acid leaching studies on alumina supported platinum-rhenium catalysts showed rhenium is again reduced to Re⁴⁺ after reduction at 482°C [3]. However, temperature-programmed reduction experiments carried out by McNicol [5] indicated platinum and rhenium were independently converted to their metallic state at 280°C and 550°C respectively. Further support for these results was provided by isothermal reduction of the catalysts at various temperatures for one hour. No interaction between platinum and rhenium was observed during reduction.

Recently, Wagstaff and Prins [6] studied the temperature-programmed reduction of Pt-Re on chlorided alumina catalysts and discovered that both platinum and rhenium were reduced to the metallic state by hydrogen at moderate temperatures. A single peak was observed in the reduction profile and it was concluded that platinum was catalyzing the reduction of rhenium.

Interaction of Pt and Re on Reduced Catalysts

Chemisorption measurements were made on a series of platinum-rhenium catalysts reduced at 500°C for one hour [8]. The hydrogen and oxygen adsorption data obtained at room temperature for these catalysts are different from the data for mechanical mixtures of Pt/Al₂O₃ and Re/Al₂O₃. The mechanical mixtures had chemisorption behavior additive of their individual components. Thus, interaction of platinum and rhenium on the reduced catalysts is suggested. However, extensive infrared studies of Pt and Pt-Re reforming catalysts through the use of adsorbed probe molecules (CO, NO) indicated independent behavior of Pt and Re on the surface, suggesting no Pt-Re interaction [9].

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Photovoltaic Liquid Junction Electrochemical Cells

Mark Bolinger

November 5, 1980

Introduction

As a result of the recent energy situation, it has become important to find new sources of energy which are clean, safe, and inexpensive. Solar energy meets the above criteria, but efficient means of converting it into more utilizable forms have not yet been discovered. Direct conversion of sunlight to electricity is a topic of current interest.

Photovoltaic cells can be either solid state, as in semiconductor/metal devices, or liquid junction, as in semiconductor/solution devices. The latter are of greater interest to the inorganic chemist due to the fact that inorganic compounds are used both as the semiconductor and as the solution electroactive species. Control of the cell stability and optimization of the energy conversion efficiency frequently depend upon careful choice of the above compounds.

Design of photovoltaic cells

Fundamental to the operation of the photovoltaic cell is the semiconductor electrode.

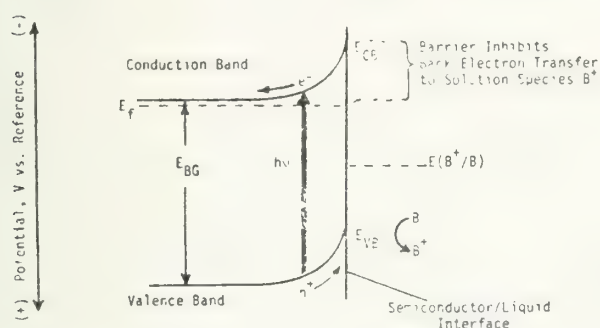


Figure 1. [10]

E_f = Fermi level

$E(B^+/B)$ = Redox potential of B.

E_{BG} = Band gap energy

e^{-1} = electron

h^+ = hole

At the semiconductor/liquid interface, charge transfer equilibration in the dark of the fermi level (electrode potential) with the redox level of the solution species produces an electric field immediately beneath the surface of the electrode [1]. The curvature of the bands in figure 1 shows the location of this electric field. Absorption of a photon excites an electron from the valence band to the conduction band. Due to the electric field, the electron (in the conduction band) and hole (in the valence band) will separate rather than decay to the ground state. The energy difference between the electron and E_{redox} is then available to do electrical work [2-5].

Prevention of the decomposition of the semiconductor electrode is crucial to the success of the photovoltaic cell. This is a problem for all semiconductors with a small band gap energy [6]. A small band gap energy is necessary for efficient utilization of the solar spectrum by the photovoltaic cell.

Strategies for achieving stable, efficient cells

Solution capture of the minority carrier (the hole in figure 1) must be made more facile than decomposition by the minority carrier. This has been accomplished in three ways. One method utilizes an electroactive species in solution which is capable of 100% efficient capture of minority carriers at the electrode surface [7-9]. Another method involves anchoring an electroactive species to the surface of the electrode [10]. A third method involves using a large band gap semiconductor which is not susceptible to decomposition. In the latter approach, the electrode is then sensitized to solar wavelengths by coating the surface with a dye which absorbs the proper wavelengths [11].

Surface states are electronic levels located at the surface with energy levels between the valence and conduction band. Surface states cause non-ideal and often detrimental behavior of the photovoltaic cell. Elimination or control of surface states must be achieved for a successful photovoltaic cell [12].

Conclusion

Solar-to-electric energy conversion efficiencies of 10-15% have begun to be realized by employing the above considerations [13]. Liquid junction cells, however, still do not achieve efficiencies as high as solid state devices.

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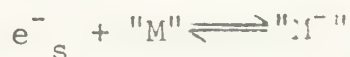
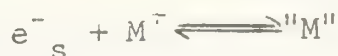
Alkali Metal Anions

Thomas Reinert

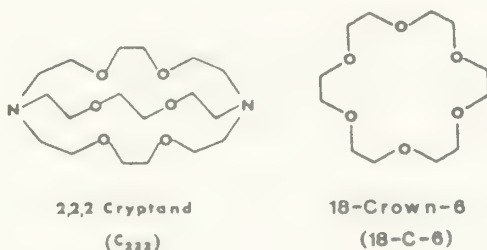
November 6, 1980

Introduction

Interest in solutions of alkali metals in ethers and amines originated in the observations of Weyl reported in 1863 [1]. Through correlation of EPR, optical spectra (UV-Vis & IR), electrical conductivity, pulse radiolysis, flash photolysis, ^{23}Na NMR, and other techniques [2], the current 3 equilibria model has been established:

Synthesis

The synthesis of alkali metal solutions is done by introducing the solvent of interest to a metal mirror formed by subliming the metal onto the walls of the reaction vessel [2,3]. This vessel must be composed of fused silica because of the presence of sodium ions in Pyrex or Kimax glass. (Note: For this reason, all work prior to 1969 should be read with a discerning eye [4].) In general, the solubility of the metal is on the order of 10^{-3}M , but is dramatically improved by the addition of chelating agents; such as, crown ethers or cryptands. The role of the chelates is to give thermodynamic stability to the solutions or films that can be formed by evaporation of the solvent [5].



This stabilization is enough to allow the formation of crystals of $(\text{NaC}_{222})^+\text{Na}^-$ upon cooling a EtNH_4 solution of Na/C_{222} (2:1) [6].

Characterization of Species

A. e^-

The bands generally attributed to e^- occur at 1400 nm in ethylenediamine for solutions of Na, Cs, or Li or for pulse radiolysis of pure ethylenediamine or NaBPh₄ in en [7]. This is blue shifted from the actual e^- band by ~400 nm [8]. This stabilization of e^- by the presence of a cation is explained as a weak ion pairing phenomenon.

B. "M"

The monomer is defined as the paramagnetic species which exhibits hyperfine coupling with the alkali metal nucleus [9] and shows a metal dependent optical band [7].

C. "M⁻"

The diamagnetic "anionic" species, which shows a metal dependent optical band, is seen in both solution and solid phase [10]. A number of models for M⁻ can be proposed; the most interesting of which is the spherically symmetric metal anion. Through interpretation of ²³Na (I=3/2) NMR [11], it can be shown that the alkali metal anion does exist in solution.

Factors effecting solution properties

It should be noted that the relative stability of each species is determined by a number of factors: "strength" of base, electron affinity of M and M⁺, temperature, relative concentration of cryptand, etc. [12].

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*Very useful paper

Chemically Modified Electrodes

Daniel R. English

November 20, 1980

The area of chemically modified electrodes is a young and rapidly expanding field in electrochemistry. The pioneering work of Lane and Hubbard [1] in 1973 led the way for many research groups to delve into the various means by which the surface of an electrode may be altered and the different paths of reactivity offered by such modification. The area has been recently reviewed [2].

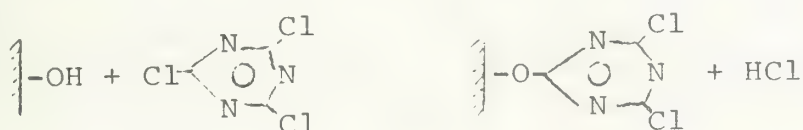
Preparation

Many methods have been developed to functionalize the surface of an electrode. These may be linked into three basic areas--covalent linkages, physical adsorption, and polymeric adsorption. The report by the Murray group [3] of reaction (1) was the first demonstration that electrode surfaces could undergo covalent



reactions with silanes. By reacting the electrode with silanes which have reactive functional groups at the other end of the molecule, further coupling reactions are possible. Investigators have used these reactive tails to tie on various electroactive moieties onto the electrode. Examples of these attached species include Ru^{II} complexes [4], ferrocenes [5], and porphyrins [6]. Wrighton's group has used silane-functionalized ferrocenes [7] to bypass the coupling reaction.

Carbon electrodes heated in the presence of O_2 have been shown to possess reactive carboxylic acid functions [8]. These acid sites may be transformed into acid chlorides and reacted with amines to form amide linkages between the electrode and amino acids [9], porphyrins [6], and ferrocenes [10] among others. Covalently-attached free-base porphyrins may be metallated by several transition metals, some of which will interact with axial bases [11]. Another useful intermediate between an electroactive species and an electrode is cyanuric chloride. The compound has been shown to undergo reactions with surface hydroxy groups on



metal oxides [12] as illustrated above. It will also couple with alcohols, primary and secondary amines, alkyl and aromatic Grignard reagents, and organic hydrazine derivatives (RNHNH_2) [12,13]. Hydroxymethylferrocene is one of the best-studied substrates to be coupled with a surface through cyanuric chloride [13].

Irreversible adsorption is another method of modifying an electrode surface. It is a much simpler procedure than covalent alteration, but the modified surface is in general less stable over a given time period [2]. Quinones [14] and porphyrins [15] have been shown to irreversibly adsorb on graphite. In an interesting variation of this procedure, Anson has prepared a "molecular anchor" [16] which has a phenanthrene and a pyridyl function connected by a vinyl linkage. A ruthenium complex containing the anchor as a ligand has been shown to adsorb on graphite electrodes [16]. Polymer adsorption to electrodes has also proven useful for attaching electroactive species to electrodes [17]. Poly p-nitrostyrene on Pt is a catalyst for O_2 reduction with the peak current for reduction being three times that on naked Pt with an estimated turnover of 10^5 [17a].

Characterization

In normal solution electrochemistry the reaction kinetics are diffusion-controlled. For the cyclic voltammetric experiment this results in a 60 mV separation in the oxidation and reduction peak potentials. Also, the peak current is linearly proportional to the square root of the scan rate. A chemically modified electrode has the reactants and products confined to the electrode. Hence, the diffusion plays no role in the electrode processes. Theory has shown [1] that for the cyclic voltammetric experiment there is no separation of the peak potentials and the peak current is linearly proportional to the scan rate. These are two major diagnostic tools in the assignment of an electrochemical response to a surface-attached species. The surface concentration of an electroactive species can be determined by utilizing the equation

$$\Gamma = \frac{Q}{nFA} \quad \text{where } \Gamma = \text{surface concentration (moles/cm}^2\text{)}$$

Q = charge passed (coulombs)
 n = equivalents per mole
 F = coulombs per equivalent
 A = area of the electrode (cm^2)

Several groups [4,12,16] have related the surface coverage to an estimate of the number of layers of the modifying group on the electrode by approximating the area of one molecule of the modifier using space-filling models. One can also use successive scans over a several minute time period to illustrate the increasing concentration of an adsorbing species on an electrode [16].

X-ray photoelectron spectroscopy (ESCA) has proven to be an invaluable tool in characterizing intermediates and products of derivitization reactions. Since its introduction in this area in 1975 by Murray [3] it has been used in several studies [6,11,14] to indicate the presence or absence of certain types of atoms. For instance one can show the presence of an amine type nitrogen and silicon on tin oxide after coupling with $(CH_3O)_3Si(CH_2)_3NH(CH_2)NH_2$ [3]

In a clever study of the binding of tetra-*m*-NH₂-phenyl-porphyrin to an acid chloride-modified graphite surface, the authors functionalized the uncoupled ortho-amino group with a nitro-containing acid chloride and used the relative areas under the nitro and amine nitrogen peaks in the ESCA spectrum to estimate the number of bonds between the porphyrin and the graphite surface [6].

Applications

The emphasis in the field of chemically modified electrodes is gradually passing from preparation and characterization to specific applications. One of the earliest of these applications was the synthesis of a chiral electrode covalently linking an enantiomerically pure isomer of phenylalanine to graphite [8]. This electrode was subsequently used to reduce *p*-acetylpyridine to the corresponding optically active alcohol with an optical purity of 15%. Two control experiments, one using the amino acid in solution and the other using an acid chloride-modified graphite electrode, yielded no asymmetric induction. This lent credence to the theory that the optical activity of the product was due to the chirality of the surface.

A second application was an attempt to reduce coordinated N₂ in acidic medium. The authors covalently attached a molybdenum-dinitrogen complex to tin oxide via a silylcyanide complex which can ligate to molybdenum. They hoped to couple an oxidation of N₂ by RX (where R = H, alkyl) with a reduction from the electrode to achieve an electrocatalytic reduction of N₂. Unfortunately, the reaction of the unattached Mo-N₂ complex with ethyl bromide in THF led to displacement of the nitrile from the complex. Reactions of electrode-bound N₂ complexes with acids have unfortunately not been reported. This would seem to be an interesting and potentially fruitful extension of the existing work.

An electrode derivitized with polyvinylferrocene (PVF) has been proposed [19] to serve as a reference electrode in nonaqueous solvents. The electrode is prepared by reducing a CH₂Cl₂ solution of PVF to the ferricinium salt which deposits on the electrode. Such polymer-modified electrodes have been shown to possess stability as a reference in acetonitrile over 21 hours [19], but the potential drifts rapidly in such solvents as benzonitrile, DMF, and methanol. The proposal by Gagné [20] to use ferrocene as an internal standard which can then be referenced to some other couple (SCE, NHE, etc.) appears to be a much simpler method to overcome liquid junction potentials and other problems inherent in electrochemistry performed in nonaqueous solvents.

The most active area of application of chemically modified electrodes has been that of O₂ reduction. This reaction is of interest because of its potential use in a non-polluting fuel cell. O₂ is reduced by two electrons to H₂O₂ at a considerable overpotential on bare electrodes [2] and efforts have been directed towards catalyzing a four-electron reduction of O₂ to H₂O. Initial

reports showed that various porphyrins [22,23,24] and phthalocyanines [24,25] both in solution and attached to electrodes are capable of catalyzing a two-electron reduction of O_2 . The peak current was greater and the peak potential was less negative for these systems than for bare electrodes. The first report of a four-electron transfer reduction of O_2 was reported in 1979 by the Collman and Anson groups. A series of covalently linked face-to-face porphyrins were synthesized [15] and shown to catalyze O_2 reduction when irreversibly adsorbed to a graphite electrode. One of the reported compounds was capable of reducing O_2 to H_2O with virtually no detectable production of H_2O_2 . The four-electron reduction was shown to be a function both of the spacing between the porphyrin planes and the metals within the porphyrin macrocycle. A second report has since been published [26] concerning another system capable of the complete reduction of O_2 by the Kuwana group. It consists of an iron porphyrin covalently bound to methyl acryl chloride polymer which is then irreversibly adsorbed on a graphite electrode. This system is much simpler to prepare than the face-to-face porphyrins but has been characterized to a lesser degree.

In conclusion, the area of chemically modified electrodes is expanding greatly and characterization of qualitative results is gaining some degree of sophistication. However, understanding of spatial and dynamic aspects of a modified surface are scarce at best. There is a great need for invention of new physical techniques to probe the surface state in these systems. The results obtained to date are nevertheless forerunners of many exciting applications to come.

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18

Nuclear Quadrupole Double Resonance Spectroscopy:
Studies of Hydrogen Bonding and Metal-Nitrogen Interactions

D. André d'Avignon

Final Seminar

November 25, 1980

A renewed interest in nuclear quadrupole resonance spectroscopy has occurred in the past 10 years. This attention stems primarily from the advent of double resonance methods capable of observing with high sensitivity the weak quadrupole signals [1]. Through these new techniques, it is now possible to obtain NQR information from the light elements present in chemically interesting molecules. The research presented here involves use of the double resonance by level crossing (DRLC) technique to investigate ^{14}N and ^2H field gradients in several groups of compounds.

A significant part of the author's research involved the partial design and construction of an NQR spectrometer. This work resulted in an automated and flexible instrument capable of performing DRLC and other sensitive double resonance experiments with about 300 mg of sample.

The ^{14}N and ^2H quadrupole resonances were determined for three polymorphic forms of anthranilic acid. NQR parameters support preconceived ideas regarding structural differences between the solid state configurations. The ^2H results are especially revealing as they reflect the extensive hydrogen bonding present in the solid material. Multiplet structure and double quantum transitions are observed for the ND_2 group. These observations are attributed to dipolar coupling between the two closely spaced deuterons [2].

^{14}N NQR studies were carried out on a series of divalent metal anthranilates. Qualitative trends observed for nitrogen field gradients suggest that upon coordination substantial amine lone pair density is removed, especially when soft metals are involved. NQR parameters are consistent with a modified Townes-Dailey model involving tetrahedral coordination about the amino nitrogen site [3].

A final study involved ^{14}N NQR investigations of square planar palladium diethylenetriamine complexes. Results from a limited number of compounds suggest the presence of electronic interactions consistent with those associated with the "trans-effect".

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"Electron Dynamics of Transition Metal-Semiquinone Complexes"

Michael Lynch

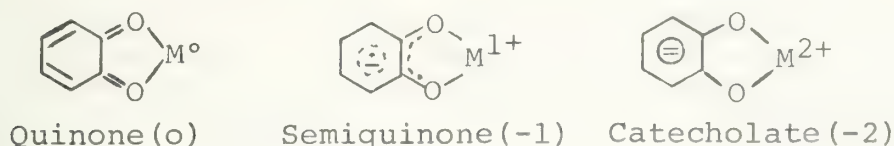
Final Seminar

December 4, 1980

Introduction

Transition metal centers interact with quinones in biological electron transfer processes, particularly photosynthesis and respiration. [1,2] An understanding of metal quinone interactions at a fundamental level is essential to the elucidation of biological electron transfer mechanisms and is the impetus for this study.

Orthoquinones as a family of ligands may bond to a metal ion in three redox-active forms:



The semiquinone form of the ligand is unique in that it is a radical species with an unpaired electron residing in a π -orbital. [3] Discussions of transition metal complexes containing the semiquinone ligand have appeared. [4] However, the formulation of these compounds as metal-semiquinone complexes has been questioned. [5,6]

Magnetic Exchange of Metal-Semiquinone Complexes

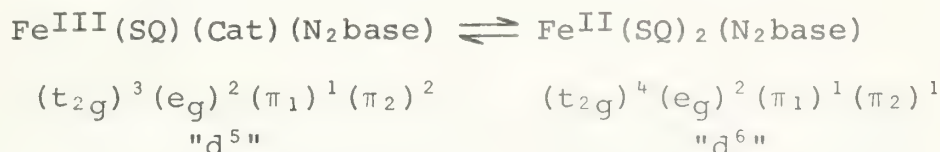
In the present study, nickel and cobalt complexes were chosen to demonstrate that weak antiferromagnetic exchange interactions can exist between paramagnetic-metal centers and coordinated semiquinones. Several nickel and cobalt complexes were studied by variable temperature magnetic susceptibility and infrared and electronic spectroscopies. The x-ray crystal structures for the [Co(II)bis(3,5-di-tert-butyl-1,2-benzosemiquinone)] tetramer and the [Ni(II)bis(9,10-phenanthrenesemiquinone)bis(pyridine)]·pyridine monomer will be discussed. As a result of these studies the materials can be unambiguously described as containing divalent metal ions and coordinated semiquinones. The magnetic exchange interactions, as gauged by the isotropic spin Hamiltonian $\hat{H} = -2J\hat{S}_i \cdot \hat{S}_j$, were found to be antiferromagnetic. In a study of several first-row transition metal complexes trends in the magnitude of the exchange interactions were observed. When the metal ion is varied the following trend results: $\text{Cr} > \text{Mn} > \text{Fe} > \text{Co} > \text{Ni}$. The trend $(3,5\text{-di-tert-butyl-1,2-benzosemiquinone}) > (9,10\text{-phenanthrenesemiquinone})$ is the result of varying the semiquinone. [7]

Electron dynamics of Manganese complexes

The compound [Mn(IV)bis(3,5-di-tert-butyl-catecholato)bis-(pyridine)]·2 pyridine (I) was obtained by reacting the [Mn(II)-bis(3,5-di-tert-butyl-1,2-benzosemiquinone)] tetramer with pyridine. Studies of (I) by several spectroscopic techniques, including x-ray crystallography, support its formulation as an Mn(IV) complex containing the catecholate form of the ligand. The fact that (I) exhibits thermochromic behavior in solution was confirmed by its variable temperature electronic spectrum. An explanation of this behavior and some interesting epr observations will be discussed in terms of the electronic and molecular structures of the molecule.

Iron Semiquinone-Catecholate Complexes

An interesting series of molecules was obtained via the following reaction: $\text{Fe}^{\text{III}}(\text{semiquinone})_3 + \text{N}_2\text{base} \rightarrow \text{Fe}(\text{"quinone ligand"})_2(\text{N}_2\text{-base}) + \text{quinone}$, where N_2base is a bidentate nitrogen base and "quinone ligand" is (3,5-di-tert-butyl-o-benzoquinone) or (9,10-phenanthrene quinone). A formulation of the complexes consistent with the observed properties is an organic mixed valence complex described here as an $\text{Fe}(\text{III})(\text{semiquinone})(\text{catecholate})(\text{N}_2\text{base})$. An intervalence transfer band is observed in the solid and in solvents of low polarity. This indicates that the material may be described as a class II compound in the Robin & Day classification scheme. [8] In polar solvents a dramatic change in the electronic spectrum was observed, indicating a change in electronic structure. It is postulated that the following reversible intramolecular electron transfer occurs:



Note that the mixed valence ferric semiquinone-catecholate complex changes to a ferrous bis-semiquinone complex. A similar change had previously been observed for a cobalt complex by Pierpont and co-workers. [9]

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Neutron Inelastic Scattering: A New Method for Studying Magnetic Exchange

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December 11, 1980

Neutron inelastic scattering is a useful tool for the study of molecular motions in liquids and solids, and for the study of long-range magnetic properties of solids. [1] This technique has recently been applied to the study of short-range magnetic exchange interactions in isolated clusters of paramagnetic transition metal ions. [2] Inelastic neutron scattering is particularly useful in this area in that it provides a direct observation of the magnetic exchange interaction.

Magnetic Exchange [3,4]

Magnetic exchange is a result of the interaction of unpaired electrons on proximate paramagnetic species. In the case of isolated clusters of paramagnetic transition metal ions, the magnetic exchange interaction can usually be described quite well by the isotropic exchange Hamiltonian,

$$\hat{H}_{\text{ex}} = -2 \sum_{\substack{i,j \\ i \neq j}} J_{ij} \hat{S}_i \cdot \hat{S}_j$$

where the sum is taken over all interacting paramagnetic ions in the cluster. The strength of the exchange interaction is gauged by the exchange parameter J_{ij} ; \hat{S}_i is the spin operator for the i^{th} paramagnetic ion.

The exchange parameter can be experimentally determined by a variety of spectroscopic and physical techniques including variable temperature magnetic susceptibility, heat capacity, electron paramagnetic resonance, and optical studies. The former two methods measure bulk properties of the sample and do not provide a direct measurement of the exchange interaction. Although the latter two techniques can be used to measure the exchange interaction directly, both have strong limitations. The EPR technique can only be used when the exchange interaction is small enough (ca. 0.3 cm^{-1}) to allow EPR transitions between the exchange-split spin states. Absorption and emission bands in optical spectra are often too broad to resolve any effects of magnetic exchange. Inelastic neutron scattering, however, provides a direct observation of the exchange parameter for very weak (ca. 2 cm^{-1}) to very strong (ca. 500 cm^{-1}) exchange interactions. In addition, these observations can be made as a function of temperature.

The Neutron Inelastic Scattering Experiment [5,6]

As the name implies, the neutron inelastic scattering technique takes advantage of the ability of thermal neutrons to interact with a sample and gain energy from, or lose energy to the sample. Since the neutron possesses a magnetic moment it can interact with the magnetic field caused by unpaired electrons in the sample. This magnetic interaction can result in the inelastic scattering of neutrons; the neutron energy gain or loss corresponds to the energy difference

between the magnetic exchange-split spin states. Analysis of the incident energy of a monochromatic (single-velocity) beam of neutrons, followed by analysis of the energies of the scattered neutrons yields a direct determination of the magnetic exchange interaction. The intensities of the inelastically scattered neutrons are described by the cross section for magnetic scattering. [7]

Specific Applications

Inelastic neutron scattering has been applied to only a handful of isolated clusters of paramagnetic ions. The deuterated copper(II) acetate monohydrate dimer was studied and was shown to have a temperature independent exchange splitting of $298(4) \text{ cm}^{-1}$. [8] Note that nearly total deuteration is necessary due to the ability of hydrogen atoms to inelastically scatter neutrons via neutron-proton interactions. The exchange parameter of deuterated acid rhodo chromium chloride $[(\text{ND}_3)_5\text{Cr}(\text{OD})\text{Cr}(\text{ND}_3)_5]\text{Cl}_5 \cdot \text{D}_2\text{O}$ was found to be slightly temperature dependent. [9] Inelastic neutron scattering has also provided the most detailed analysis of the exchange interaction in the tetrameric cluster rhodoso chloride $[\text{Cr}_4(\text{OD})_6(\text{ND}_3)_{12}]\text{Cl}_6 \cdot 4\text{D}_2\text{O}$. [10] It is hoped that further detailed analyses can provide insight into the mechanisms that give rise to magnetic exchange interactions.

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EPR Studies of the Jahn-Teller Effect

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January 27, 1981

In 1937, Jahn and Teller proposed the existence of an inherent instability with respect to nuclear displacements for orbitally degenerate electronic states [1]. Since the original premise was put forth, the so-called Jahn-Teller Theorem has become a widely invoked and controversial phenomenon. This debate has led in recent years to numerous experimental studies on molecules directed towards the observation of the predicted theoretical behavior.

Theoretical Considerations [2-4]

Although the dependence of molecular Hamiltonians on nuclear coordinates is often neglected, it is exactly this which leads to the Jahn-Teller Effect (JTE). It is possible for certain normal modes of a molecule to couple with the electronic states, leading to a linear dependence of electronic energies upon nuclear displacements. Applying a linear perturbation of this kind to an E-type degenerate state leads to the "Mexican hat" potential surface and removal of the electronic degeneracy.

In the case of a large vibronic coupling, quadratic terms in the interaction must also be included. These additional terms result in a modified "Mexican hat" potential having three equivalent minima. These minima, in the case of octahedral symmetry, correspond to the three possible tetragonal distortions. In the presence of asymmetric lattice forces the minima may become non-equivalent. In either case, the potential surface may be characterized by the parameters E_{JT} , R_{JT} , B and δ [5].

Observation of the JTE

Optical spectroscopy, structural studies and EPR have been useful in characterizing Jahn-Teller (JT) distortions [5]. In optical spectroscopy of transition metal complexes, the effect may be inferred from observed splittings in absorption bands associated with $d \rightarrow d$ excitations [6,7]. If the splitting patterns are properly assigned, the JT stabilization energy (E_{JT}) may be obtained. The determination of the JT radius (R_{JT}), in the case of static or dynamic distortions, is obtained through structural studies in the measurement of bond lengths or vibrational amplitudes [5,8,9].

The first observation of the JTE using EPR was noted in 1950 [10]. The transformation of the spectrum from isotropic to anisotropic upon lowering the temperature is an indication of the Jahn-Teller Effect. The dynamics are extremely dependent on the surrounding lattice of the distorting complex and cooperative effects may be important [11].

Silver and Getz, in a study of $\text{Cu}(\text{H}_2\text{O})_6^{+2}$, proposed for this complex the existence of a dynamic JTE at very low temperature [12]. Having examined the variation in the g and A tensors as well as linewidth as a function of temperature, these authors proposed a

three site model with rapid exchange among distortions. From their data, estimates were made of the energy separating the minima for the three distortions (δ) and of the barrier height to interconversion (B).

Ammeter, et. al. [5] reviewed existing data on twelve compounds with a "CuN₆" core (N = tach, en, bpy, phen and NO₂⁻); all of these compounds showed either static or dynamic JT behavior. The uniformity among the values of the parameters examined has led to the conclusion that only the local "CuN₆" fragment need be considered in describing the JTE in these complexes.

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Applications of Nuclear Quadrupole Double Resonance Spectroscopy

Les Butler

February 5, 1981

Nuclear quadrupole double resonance (NQR) spectroscopy can yield direct information about the nature of chemical bonding at a particular quadrupolar nucleus ($S \geq 1$) in a molecular crystal. However, due to experimental difficulties related to the low transition frequencies generally associated with the light nuclei (^2D , ^{10}B , ^{11}B , ^{14}N , and ^{17}O) and, in the case of ^{17}O , the low natural abundance, the contribution of NQR spectroscopy to our understanding of chemical bonding has been small. Only recently have nuclear quadrupole double resonance techniques been developed to facilitate observation of NQR spectra of the light elements.[1]

To further advance the field of NQR spectroscopy, a new instrument was constructed in collaboration with D. Andre D'Avignon. It employs the established technique of nuclear quadrupole double resonance by adiabatic demagnetization in the laboratory frame (ADLF). By this technique, NQR spectra in zero applied magnetic field can be obtained from 500 mg or less of polycrystalline material. Several instrumental functions are under computer control, resulting in nearly total automatic operation. In addition, variable temperature operation in the range of 20-300 K is also feasible.

NQR spectroscopy provides information about the electric field gradient about a quadrupolar nuclei. Since the elements of the electric field gradient tensor are determined by the electric charge distribution in the molecule, details of chemical bonding can be obtained.[2] In this work, ^2D and ^{17}O NQR spectra were obtained on a wide variety of inter- and intramolecular hydrogen bonds. The experimentally obtained electric field gradient parameters were interpreted by a theoretical analysis of the formaldehyde-water hydrogen bonding interaction. Large changes in the electric field gradient parameters were observed at the deuterium and oxygen sites.

The first complete NQR spectrum for an $S=3$ spin system, ^{10}B , has been obtained from a study of boric acid. Techniques developed in this work have been applied to the study of the ^{10}B and ^{11}B NQR of decaborane(14) and ortho-carborane.

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Detection and Applications of Multiple Quantum NMR

Peter Doan

March 3, 1981

Nuclear magnetic resonance spectroscopy is one of the most powerful physical methods available to chemists. Advances in pulse techniques and magic angle spinning experiments have extended the range of compounds that can be studied by NMR. Recent advances in multiple photon (multiple quantum) NMR allow the detection of "forbidden" transitions and shows these transitions contain information complimentary to single quantum (SQ) NMR.

I. Detection

Continuous wave experiments have been used to observe multiple quantum transitions since Anderson first reported a double quantum spectrum in 1956 [1]. The technique, which works best for strongly coupled spin systems, is to increase the rf intensity just enough to power saturate the single quantum spectrum. This method usually produces a low resolution double quantum spectrum. Even greater rf intensity power saturates the DQ spectrum but does not lead to higher order MQ transitions [2]. Thus the versatility of the cw multiple quantum experiment is severely limited [3].

Simple time domain experiments such as the pulse techniques used in ^{13}C NMR can not observe multiple quantum transitions. The selection rules for observing transverse magnetization are strictly $\Delta m_I = \pm 1$. The use of two dimensional NMR spectroscopy allows a method to circumvent the selection rules [4-8]. However, the complexity of the experiment does not allow a brief overview.

II. Applications

The most straightforward use of MQ spectra is for spectral assignment and simplification [6,9]. High order spectra even for complex molecules are simple and easy to assign. By using the information in the N-1 and N-2 quantum spectra, where N is the maximum change in m_I , most of the coupling constants of the molecule can be found. This method is analogous to using isotopic substitution to remove some of the spectral complexity [10].

MQ experiments can also contain information on relaxation and molecular correlation not found in SQ spectra [11]. An example of this is the possibility of correlation between two rotating methyl groups. If there is no correlation (independent rotation) the 4 quantum region of the spectrum will contain five lines from the methyls. Any perturbation on that five line will show partially coupled rotation [12].

Multiple quantum transitions can also be of great use in $I > \frac{1}{2}$ nuclei. NMR spectra of these nuclei in solids have linewidths dominated by quadrupolar splitting and relaxation. The highest order MQ transition is insensitive to first order quadrupole interactions [3]. This technique has been applied to only $I=1$

nuclei (^2H and ^{14}N) in single crystals. Double quantum NMR of deuterium in powders can be done by combining the double quantum technique with magic angle spinning [13]. The resulting spectrum is high resolution and relatively insensitive to small variations in the spinner angle. Further enhancement of the spectra of these nuclei can be obtained by various cross-polarization techniques [14,15].

A complimentary method to deuterium DQ NMR in solids is proton NMR in 99.5% deuterated compounds using deuterium double quantum decoupling. The proton linewidths in solids and liquid crystal solvents of these molecules are dominated by coupling to the deuterium. One way to decouple the deuteriums is to cause a $| -1 \rangle \leftrightarrow | +1 \rangle$ transition since the $| 0 \rangle$ spin state does not couple to the proton spin [16,17,18].

Another use of MQ NMR is in the determination of nuclear quadrupole coupling constants in short lived beta decay nuclei e.g., ^8Li and ^{12}B . By monitoring the electrons emitted from such nuclei when placed in a magnetic field an asymmetry develops from the different spin states of the nuclei. Inducing saturation of transitions causes a drop in asymmetry. Multiple quantum transitions cause much greater changes in the asymmetry and yield more accurate determination of the NQC [19,20].

Though multiple quantum NMR is still a very new physical method and has not been applied to many systems, the potential for it is great. The techniques are especially applicable to inorganic systems where quadrupolar nuclei make the observation of "normal" SQ NMR difficult.

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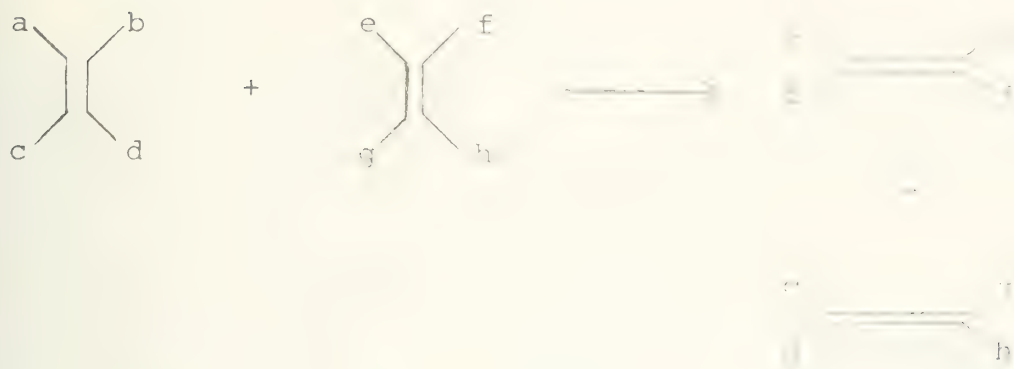
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Recent Developments in the Olefin Metathesis Reaction

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The first olefin metathesis reactions were reported in 1957. Today applications include production of higher olefins, synthesis of polymers important to the plastics industry, and most recently synthesis of biologically active molecules such as insect attractants. It is now apparent the mechanism proceeds through a metal carbene intermediate [1].

Initiation

There is growing evidence that initiation steps for the metathesis reaction are quite different from propagation steps. The reaction is catalyzed by a variety of catalysts and initiation mechanisms may be expected to be different for each catalyst type.

A. Catalysts with Stable Metal Carbene Ligands

In general these catalysts are the stable Fischer-type carbenes and exhibit sluggish, if any, metathesis activity. Destabilization of the carbene results in a more active catalyst [2]. A vacant site is clearly important for coordination of olefin and rapid metathesis [1a].

B. Catalysts Without Stable Metal Carbene Ligands or Organometallic Co-catalysts

Initiation mechanisms for these types of catalysts are considerably less well-understood. One possible mechanism proceeds through a π -allyl metal hydride intermediate [1a,3], although this has not been conclusively demonstrated [4]. In a mechanism pertinent to alumina-supported metal carbonyls the active carbene is thought to originate from oxidative addition of surface alcohol to a chemisorbed metal carbonyl fragment [5].

C. Catalysts with Organometallic Co-catalysts

The primary initiation mechanism for these types of catalysts involves alkylation of the transition metal followed by α -elimination to generate the reactive carbene [6]. In this case anomalous

olefins corresponding to the first turnover of the catalyst can be detected in the initial stages of the reaction [7].

Role of Organometallic Co-catalyst

Recently it has been demonstrated in certain systems that the aluminum co-catalyst serves to stabilize the reactive carbene by formation of a methylene bridged titanium aluminum complex [8]. Without the aluminum reagent, the position of the equilibrium between the carbene and metallocyclobutane favors the metallocyclobutane [9].

Propagation and Competing Processes

Decomposition of the metallocyclobutane by a variety of processes in addition to metathesis has been observed [10]. The reductive elimination to cyclopropane products is reversible, thus accounting for the generally small yields of cyclopropane products in metathesis systems [11]. Homologation competes effectively with the metathesis reaction. The predominance of metathesis over homologation in certain systems has been related to the metal carbene bond strength [12]. β -hydrogen transfer is more rapid than metathesis in one system [8a,13].

Metathesis by Transition Metal Oxide Complexes

Several early transition metal catalyst systems containing carbene and metal-oxo moieties have been reported [14]. Ab initio calculations [15] and limited experimental evidence suggest that metallocycle formation is driven by the formation of a metal-oxygen triple bond. A vacant coordination site may also be necessary [14b, 14c].

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Zeolite-Supported Transition Metal Carbonyls

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The concept of supporting transition metal complexes on zeolites is of great interest in that such complexes have long been proposed as reactive intermediates in zeolite catalysis. The past decade has seen a considerable amount of work in this area, with particular emphasis upon first row transition metal complexes of amines, nitrosyls, and isocyanides. Several reviews have appeared [1-3]. Although it has been known for several years that carbon monoxide does adsorb onto most zeolites containing metal ions, active interest in supported metal carbonyls has been relatively recent. The majority of work in this field has been published within the past five years, and has principally involved zeolites X and Y. These are the synthetic analogues of the naturally occurring zeolite, faujasite.

Faujasite Zeolites-Structure and Properties [4-6]

The framework of a zeolite is an anionic aluminosilicate structure consisting of tetrahedral SiO_4 and AlO_4 units linked through common oxygen atoms. The basic building block of the faujasite framework is the sodalite unit, or truncated octahedron. This is a 24-vertex polyhedron, with Si or Al atoms at each vertex, which has a total of 14 faces, six square and eight hexagonal. Each sodalite unit is linked to four others through hexagonal faces in a tetrahedral geometry. The faujasite framework thus contains three types of cavities: hexagonal prisms, the sodalite cavities, and larger units known as supercages. Each supercage has an inner diameter of approximately 13 \AA , and is connected to four other supercages through 8 \AA apertures. The faujasites are thus termed "large pore" zeolites, the supercage networks being considerably larger than the pores of most other known zeolites. The synthetic X and Y faujasites are distinguished by their framework Si:Al ratio, which varies between 1 and 1.5 for X and from 1.6 to 3 for Y.

The anionic charge of the framework is balanced by cations, usually metal ions, which reside in the zeolite cavities. In dehydrated zeolites the cations are generally located in or near the small cavities, where coordination to framework oxides is maximized. The water present in hydrated zeolites draws a substantial number of cations into the supercages where aquo complexes can be formed. Such zeolites can usually be dehydrated by vacuum treatment at approximately 400°C . Zeolite cations can be exchanged, most often by simple treatment with an aqueous solution of the new cation. Hydrogen zeolites contain protons instead of metal ions. They are somewhat acidic due to framework hydroxyl groups, in contrast to the basic character of metal ion zeolites.

Preparation and Characterization of Supported Metal Carbonyls

Two basic methods have been used to prepare zeolite-supported transition metal carbonyls. The first involves the treatment of a transition metal ion-exchanged zeolite with carbon monoxide. The other method employs direct adsorption of a metal carbonyl compound onto the zeolite, usually by sublimation.

It has been known since the 1960's that CO adsorbs onto Group IA, IIA, and (2+) transition metal ion-exchanged zeolites [7]. The adsorption, however, is quite weak. Facile desorption is achieved by room temperature evacuation. The metal ion-CO interactions have been specifically identified as weak by the observation of high frequency carbonyl bands in the IR ($2220-2160\text{ cm}^{-1}$) and by X-ray determinations of very long M-C bonds. More stable metal carbonyls have been obtained using transition metal ions in lower oxidation states. Schomaker has reported the formation of a Ni(I) carbonyl species on Y zeolite by reduction of $\text{Ni}^{\text{II}}\text{Y}$ to $\text{Ni}^{\text{I}}\text{Y}$ with Na vapor, followed by treatment with CO [8]. CO desorption required evacuation at temperatures no less than 200°C . Huang has reduced $\text{Cu}^{\text{II}}\text{Y}$ to $\text{Cu}^{\text{I}}\text{Y}$, and observed a Cu(I) carbonyl after CO adsorption which was stable to room temperature evacuation [9]. Cu(I) zeolite samples treated with CO after adsorption of amines showed IR bands between 1900 and 2100 cm^{-1} . These have been assigned to Cu(I) carbonyl amine complexes in the zeolite supercages. Primet has used ESCA and IR spectroscopy to characterize a Y faujasite-supported Rh(I) dicarbonyl species [10]. The dicarbonyl was formed by CO/ H_2O reduction of $\text{Rh}^{\text{III}}\text{Y}$, and was stable to room temperature evacuation. More strenuous reduction of transition metal ions in zeolites has generally resulted in the formation of metal particles instead of neutral carbonyls [11,12]. Zanobi, however, has reported the synthesis gas reduction of Rh(III) in a Y zeolite to a rhodium carbonyl cluster [13].

Gelin has adsorbed $\text{Rh}_6(\text{CO})_{16}$ onto NaY zeolite [14]. Decarbonylation by O_2 followed by recarbonylation gave same Rh carbonyl species observed by Zanobi, believed by its IR spectrum to be a zeolite-entrapped cluster. A similar experiment using an alumina support yielded only a Rh(I) dicarbonyl. Gelin has speculated that the zeolite supercages prevent Rh oxidation. Verbllovskii has studied the thermal decomposition of $\text{Ni}(\text{CO})_4$ on an X faujasite [15]. A quantitative measurement of decarbonylation indicated the formation of a stable Ni monocarbonyl species during the decomposition. Total decomposition produced Ni metal. Tkatchenko has adsorbed $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$ onto HY zeolites [16]. IR evidence has been obtained for an initial H-bonding interaction between the carbonyl ligands and zeolite hydroxyl groups. Partial thermal decomposition of adsorbed $\text{Fe}(\text{CO})_5$ resulted in loss of one equivalent of CO and production of adsorbed $\text{Fe}_3(\text{CO})_{12}$. This has been postulated to occur through the intermediacy of zeolite-stabilized $\text{Fe}(\text{CO})_4$ units. Total decomposition of the Fe carbonyls yielded Fe(II) and H_2 , similar to work by Gallezot with $\text{Mo}(\text{CO})_6$ [17]. Decomposition of $\text{Re}_2(\text{CO})_{10}$ and $\text{Ru}_3(\text{CO})_{12}$ on HY, however, resulted in the production of metal, as observed above for $\text{Ni}(\text{CO})_4/\text{X}$.

Catalysis involving Supported Metal Carbonyls

Examples of heterogeneous catalysis observed to involve zeolite-supported carbonyls are rare. Zanolí has reported his proposed rhodium carbonyl cluster supported on Y faujasite to be an active and stable hydroformylation catalyst [13]. $\text{Rh}^{\text{III}}\text{X}$ and $\text{Rh}^{\text{III}}\text{Y}$ zeolites are known to be active catalysts in methanol carbonylation. Anderson and Scurrall have obtained IR evidence for production of a $\text{Rh}(\text{III})$ acyl after treatment of $\text{Rh}^{\text{III}}\text{X}$ with CO and CH_3I [18,19]. This is analogous to homogeneous studies. No acyl was produced by similar treatment of $\text{Rh}(\text{III})$ on silica, which is known to be much less active in carbonylation catalysis than the zeolite systems.

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Design and Characterization of One-Dimensional Inorganic Conductors Containing Metallomacrocycles and Polyhalides

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One dimensionality is ascribed to materials that exhibit pronounced physical properties in one direction as compared to the orthogonal directions. Intense interest in solids with one-dimensional electrical conductivity has developed in the past 10 to 15 years because of their uniqueness as well as their potential for practical application [1-3]. Much of the impetus for this current interest came from measurement of one-dimensional conductivity in certain polymeric, organic, and inorganic substances in the 1950's and 60's. Significant inspiration also was provided by the prediction of W. A. Little in 1964 that it should be possible, on theoretical grounds, to synthesize a substance that would exhibit one-dimensional superconductivity at room temperature [4].

Background

The largest class of inorganic one-dimensional (1-D) conductors have in common an important structural feature: stacked, planar metal-ligand units arranged in segregated columns with the metal atoms forming a linear chain at the center of each column. The most thoroughly studied member of this class is Krogmann's salt, $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.4}\cdot 3\text{H}_2\text{O}$, $[\text{KCP}(\text{Br})]$ [2,5]. Its conductivity is associated with a partially filled energy band that forms on close approach and partial oxidation of the $\text{Pt}(\text{CN})_4^{2-}$ units.

Although $\text{KCP}(\text{Br})$ and other 1-D conductors often are called "molecular metals", the temperature dependence of their conductivities is markedly different from that of metals. A model that relates conductivity to two temperature-dependent parameters, carrier concentration and carrier mobility, has been developed by Epstein, Conwell, and Miller and successfully applied (for $T > 70\text{K}$) to a number of 1-D organic conductors exhibiting a variety of conductivity-temperature dependencies [6].

Because conventional band theory cannot adequately account for many properties peculiar to 1-D conductors, such as the variation of conductivity with temperature, most theoretical treatments of these systems apply the Hubbard model, which describes electron motion in crystalline solids in terms of intersite electron transfer and intrasite electron-electron Coulomb repulsion [2,7].

Design of 1-D Inorganic Conductors

Numerous attempts have been made to design new 1-D inorganic conductors based on the experimental findings and theoretical models that have emerged from the studies of $\text{KCP}(\text{Br})$ and organic conductors of analogous columnar structure. Recent successes involve partial oxidation of planar metallomacrocyclic units with iodine or bromine [8-16].

Ligands include diphenylglyoximate (dpg) [8,10,11,13], benzoquinone-dioximate (bqd) [8-10], phthalocyaninate (Pc) [10,14,15], and an octa-methyltetraabenzporphyrinate (OMTBP) [16]. These ligands have been combined with various metals, but principally Pd and Ni. In a more recent variation on this approach, the metallomacrocycles are covalently linked by either oxygen [17,18] or fluorine [19] atoms in a face-to-face orientation to form oligomers prior to oxidation.

Characterization of 1-D Conductors

A principal goal in the investigation of the 1-D systems described above has been elucidation of the relationship of conductivity to molecular composition, structure, and degree of partial oxidation of the metal-ligand unit. The characterization of these materials thus has included conductivity measurements (on single crystals when possible), crystal structure determinations, and identification of the form of halide present. All of the reported x-ray crystal structures consist of stacked planar metal-ligand units and parallel chains of halogen atoms [11-16]. Room temperature single crystal conductivities as high as $750 \text{ (ohm cm)}^{-1}$ in the direction parallel to the stacking axis have been measured [15]. For the iodine-containing substances, the form of the iodine has been determined by resonance Raman and iodine Mössbauer spectroscopy [10-12,14-19]. Resonance Raman has also been applied to the bromine-containing materials [13]. Assignments are based primarily on comparison to spectra of well-characterized model compounds.

Insight into the nature of the charge transport in Ni(Pc)I_x [14,15] and Ni(OMTBP)I_x [16,20] has been provided by measurement of variable temperature conductivity, magnetic susceptibility, and esr spectra.

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Synthesis and Reactivity of Transition Metal Organometallic and Heterobimetallic Complexes

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The preparation of cyclopentadienyl transition metal lithium complexes has become routine. $\text{Cp}_2\text{ReLi} \cdot \text{PMDT}$ and $\text{Cp}_2\text{MoHLi} \cdot \text{PMDT}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{PMDT} = 1,1,4,7,7\text{-pentamethyldiethylenetriamine}$) have been synthesized in high yield by the addition of one equivalent of *n*-butyllithium to either Cp_2ReH or Cp_2MoH_2 , respectively, in the presence of PMDT. $\text{Cp}_2\text{ReLi} \cdot \text{PMDT}$ has been a useful starting material in the production of Cp_2Re -alkyls and heterobimetallic compounds such as $\text{CpRe}(\text{CO})_3\text{MoCp}$ [1].

Attempts to produce other heterobimetallic systems using $\text{Cp}_2\text{ReLi} \cdot \text{PMDT}$ have been unsuccessful because of competition from a more favorable hydride abstraction reaction of the very basic Cp_2Re^- anion. For example, the reaction between $\text{Cp}_2\text{ReLi} \cdot \text{PMDT}$ and $\text{Cp}_2\text{Ta}(\text{CH}_3)_2\text{BF}_4^-$ [2] yielded Cp_2ReH and $\text{Cp}_2\text{Ta}(\text{CH}_3)(=\text{CH}_2)$ rather than a Re-Ta complex. Similarly, the reaction between $\text{Cp}_2\text{ReLi} \cdot \text{PMDT}$ and $\text{CpMo}(\text{CO})_3(\text{CH}_2)_3\text{Br}$ [3] gave a mixture of products including Cp_2ReH , but no Re-Mo compound. Substitution of $\text{Cp}_2\text{MoHLi} \cdot \text{PMDT}$ for $\text{Cp}_2\text{ReLi} \cdot \text{PMDT}$ did not yield any bimetallic products.

The reactions of $\text{Cp}'(\text{C}_5(\text{CH}_3)_4=\text{CH}_2)\text{Ti}(\text{CH}_3)$ [4] with $\text{H}(\text{CO})_3\text{MCp}$ and $\text{H}(\text{CO})_3\text{M Cp}'$ ($\text{M} = \text{Mo}, \text{W}$, $\text{Cp}' = \eta^5\text{-C}_5(\text{CH}_3)_5$) lead to a series of new bimetallic compounds. The X-ray analysis of $\text{Cp}_2'\text{Ti}(\text{CH}_3)(\text{OC})_3\text{MoCp}$ indicated one of the carbonyl ligands was bridging the Ti and Mo atom centers. The bridging CO ligand was bound to the Ti atom through the oxygen atom and to the Mo atom through the carbon atom. The length of the C-O bond in the bridging carbonyl was substantially longer (1.21\AA) than the terminal carbonyl bond lengths (1.15\AA). Also, the C-Mo bond length of the bridging carbonyl was shorter (1.87\AA) than the C-Mo bond lengths in the terminal carbonyls (1.94\AA) [5]. The changes in bond lengths indicated a reduction in the carbon-oxygen bond order as a result of coordination to $\text{Cp}_2'\text{Ti}(\text{CH}_3)$, a Ti(IV) Lewis acid [6].

The mechanism of the reaction involves the donation of H^+ from the metal hydride, $\text{H}(\text{CO})_3\text{MoCp}$, to the nucleophilic $\text{C}_5(\text{CH}_3)_3=\text{CH}_2$ ring of the Ti carbene. This H^+ transfer generates an $\eta^5\text{-C}_5(\text{CH}_3)_5$ ring and opens a coordination site on the Ti atom center. The coordinatively unsaturated $\text{Cp}_2'\text{Ti}(\text{CH}_3)$ Lewis acid is then formed and may react with a basic carbonyl oxygen to give product.

Studies on the possibility of reducing the carbonyl ligands in these compounds have not been successful. However, the Ti-Mo compound will slowly hydrogenate 1-pentene to pentane at ambient temperature and pressure.

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Chemistry of Lithiated Biscyclopentadienyl Transition Metal Hydrides

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Organolithium reagents have long been utilized for a variety of organic reactions [1]. More recently, lithium containing species have proven useful for synthesis of organometallic compounds previously unknown [2,3].

Our group has concentrated on electron rich second and third row early transition metal complexes in this regard. The low valent state of the metal is stabilized by donor ligands such as cyclopentadienide ($\eta\text{-C}_5\text{H}_5$, cp). Thus, cp_2MH_x compounds ($\text{M} = \text{Ta}$, $x = 3$; $\text{M} = \text{Mo}$, W , $x = 2$; $\text{M} = \text{Re}$, $x = 1$) have served as starting materials for lithiation in the presence of pentamethyldiethylenetriamine (PMDT) to form $\text{cp}_2\text{MH}_{x-1}\text{Li}\cdot\text{PMDT}$ (M-Li). Subsequent reaction mixtures, with a variety of organic and organometallic halides yields a complex set of reaction mixtures, with a diversity of products. Among the compounds isolated have been cp_2Re alkyls and mixed metal species with unusual bridging carbonyls. These novel compounds can be of significant interest as models of proposed intermediates in catalytic cycles such as the hydrogenation of olefins or carbon monoxide.

The nature of the TaLi intermediate has been poorly understood so far [4]. The polyhydridic nature of the starting material seriously complicates the reactions in this system. It has been shown that lithiation does not proceed to completion, and is not specific for any one hydride.

The x-ray crystal structure of $\text{cp}_2\text{TaH}_2\text{Li(PMDT)}$ has been determined. The lithium atom is chelated by the amine and is 3.11\AA from the Ta. Here it has replaced the central hydride, but this probably does not reflect completely the nature of the intermediate in solution.

$\text{Cp}_2\text{ReLiPMDT}$ has proved to be the most versatile synthetic reagent of those studied. In addition to the previously reported rhenium alkyls, a Re-Hg and a Re-Mo compound have been obtained, and have been characterized by x-ray crystallography. ReLi reacts with PhHgBr to form $(\text{cp}_2\text{Re})_2\text{Hg}$, probably by a two step process. The Hg linearly bridges the two rhenocene moieties, with a Re-Hg distance of 2.70\AA .

With $\text{cpMo(CO)}_3\text{Cl}$, ReLi gives $\text{cpReCO}(\mu\text{-CO})_2\text{Mocp}_2$, again, probably by rearrangement of the initially formed complex. The Re-Mo bond distance is 2.96\AA , and the bridging carbonyls are semi-bridging [5]. These activated carbonyls can be attacked specifically by methyllithium.

The rhenium alkyls have also been the subject of further study. The crystal structures of cp_2ReCH_3 and $\text{cp}_2\text{Re(CH}_3)_2\text{SO}_3\text{F}$ have been determined. The Re-C distances are the same (2.21\AA) in both compounds, and the $\text{CH}_3\text{-Re-CH}_3$ angle in the cation is the same as the H-Mo-H angle in cp_2MoH_2 [6].

Deuteration studies of cp_2ReR ($\text{R} = \text{H}, \text{D}, \text{CH}_3, \text{CD}_3, \text{CH}_2\text{CH}_3, \text{CH}_2\text{CD}_3, \text{CH}_2\text{CH}_2\text{CH}_3$) indicate that bonding to the electron rich metal center causes activation of the β hydrides, but this is not the only reaction pathway open to these metal alkyls. Inter-, rather than intra-, molecular mechanisms are apparently involved in the rearrangements, decompositions, and side reactions observed.

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Transition Metal Chemistry of and in Liquid Ammonia

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Though reactions of liquid ammonia have been studied for over 150 years, it wasn't until 1897 that H. P. Cady first conceived of liquid NH_3 as being a solvent. This work prompted C. Kraus and E. C. Franklin both collectively and independently to do much of the early work into NH_3 as a solvent. The publication in 1935 of Franklin's The Nitrogen System of Compounds was the culmination of his work, and the foundation for future work in the field [3,4].

Liquid Ammonia as a Solvent

Liquid NH_3 is a polar solvent, though somewhat less so than water [5]. There are several advantages to using NH_3 as a solvent: 1) alkali metals dissolve in NH_3 without reacting; 2) thermally unstable compounds can be prepared; 3) solubilities are different in NH_3 from those in H_2O ; 4) ammonolysis is less likely to occur than hydrolysis [2]. Laboratory sources of the solvent are obtained either by condensing NH_3 (g) from a pressurized tank, or if someone is really desperate, aqueous NH_3 solutions can be a source with a little bit of work. Reactions can be carried out on the benchtop, with Carius tubes, or by use of vacuum line techniques. Physical methods in liquid NH_3 solutions include both Raman and electronic spectra, electrochemical methods, chromatography, and tensiometric studies. The vapor-pressure composition isotherm is determined by a tensiometric study. From such a study the number of reacting NH_3 's can be determined as well some indication of by-products from the reaction [2].

In general the reactions of transition metal compounds in liquid NH_3 can be divided into four main areas: 1) ammoniation, where the metal is coordinated by NH_3 's; 2) ammonolysis, which is essentially the "hydrolysis" of NH_3 by NH_3 ; 3) substitution, where NH_3 replaces other ligands on the metal center; and 4) redox. Redox reactions are fairly unusual for transition metals and will not be considered here.

Ammoniation

Most metals are coordinated by NH_3 , and chemistry of the ammoniates is essentially very similar to the chemistry of hydrates of metals. Bond strengths range from an ion-dipole interaction to full coordination of the metal by ammonia. As in the case of the hydrates, not all NH_3 's have to be coordinated, and the number of NH_3 's per compound is generally dependent upon temperature. As few as one NH_3 and as many as 14 have been observed as being associated with one metal center [2]. $\text{TiCl}_3 \cdot 5\text{NH}_3$ is formulated as $\text{trans}[\text{TiCl}_2(\text{NH}_3)_4]\text{Cl} \cdot \text{NH}_3$ on the basis of thermal decomposition and IR data [6]. $\text{TiF}_4(\text{NH}_3)_2$ appears to be a cis-octahedral array on the basis of ^{19}F -NMR data [2]. $\text{TiCl}_3(\text{NH}_3)_3$ is formulated as $\text{fac}[\text{TiCl}_3(\text{NH}_3)_3]$ and

TiCl_3NH_3 appears to be a polymer with halide bridges [6]. It should be pointed out that things are not always as they might seem. $\text{VBr}_3 \cdot 6\text{NH}_3$ was originally formulated as an ammoniate; however, it really is a mixture of $\text{VBr}_2(\text{NH}_2) \cdot 4\text{NH}_3$ and NH_4Br [7].

Ammonolysis

While ammonolysis will occur in general it occurs less extensively than hydrolysis due primarily to the lower solubility of the products as compared to hydrolysis products. The charge to radius ratio on the metal center seems to be the controlling factor as to whether and to what extent ammonolysis occurs, but it is not the only factor, since Ti(III) doesn't undergo ammonolysis and V(III) does [6,7]. When TiCl_4 is added to liquid NH_3 at -36°C , $\text{TiCl}(\text{NH}_2)_3 \cdot 2\text{NH}_3$ is formed; at 25°C this is converted to $\text{TiCl}(\text{NH}_2)_3$ [8]. The extent of ammonolysis can be expanded thermally or by the use of KNH_2 . At 280°C $\text{TiCl}(\text{NH}_2)_3$ is converted to TiNCl [2,14]. Unfortunately amides and imides tend not to be of perfectly integral stoichiometry, and they also tend to be insoluble in anything but those solvents that decompose them. It is thought that many of the amides exist as polymers in the solid state [2]. There also exists evidence for ammonolysis products being anions, and anions have been observed in solution [9,10]. The cyclopentadienyl derivatives of TiCl_4 also undergo ammonolysis [11,12,13].

These amide bridges are not merely a phenomenon of the titanium halides. Amide and imide formation and the production of imide and amide bridged polymers of Co(III) have been studied as well as other examples [15,16].

Substitution

With titanium, substitution reactions have not been studied very extensively. The reactions of TiBr_3 and various alkali metal cyanides have been looked at and it has been concluded that the Ti^{3+} is in a 7-coordinate CN environment of C_{2v} symmetry [17]. The addition of ammonium cyanide to TiCl_3 results in $(\text{NH}_4)_3\text{TiCl}_3\text{CCN}$ which appears to be polymeric with bridging CN's [18].

Substitution reactions with metal carbonyls have been studied the most extensively. The reactions of cobalt carbonyl derivatives are typical of the observations that have been made. $\text{Co}_2(\text{CO})_8$ disproportionates to $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO})_4]_2$ [1]. $[\text{Co}(\text{CO})_4\text{PPh}_3]^+$ in NH_3 at -50°C forms $\text{HCo}(\text{CO})_3\text{PPh}_3 + \text{NH}_4\text{NCO}$ [1,19]. If $[\text{Co}(\text{CO})_2(\text{Ph}_2\text{PCH}_2)_3\text{CCH}_3][\text{Co}(\text{CO})_4]$ is reacted in NH_3 at 20°C , $\text{Co}(\text{CO})[(\text{Ph}_2\text{PCH}_2)_3\text{CMe}]\text{CONH}_2$ is obtained and if this is further reacted at 60°C , $\text{HCo}(\text{CO})(\text{Ph}_2\text{PCH}_2)_3\text{CMe}$ is obtained [1,20]. Spiroheterocyclic cobalt complexes have also been prepared from $\text{C}(\text{CH}_2\text{PR}_2)_4$ and $\text{K}_2[\text{Co}(\text{NO})\text{CCO}(\text{CCN})_2]$ [1,21,22].

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*review

Homogeneous Mononuclear Fischer-Tropsch Chemistry: Models and Catalysis

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The continual rising cost of oil and gas has lead chemical manufacturers to look for more economically favorable sources to produce their chemical feedstocks. Within the last decade there has been considerable interest in the utilization of synthesis gas ($\text{CO} + \text{H}_2$) derived from coal in a Fischer-Tropsch type reaction producing a wide variety of hydrocarbon products [1]. This is presently unattractive due to the costly separation and purification processes needed, resulting from the lack of selectivity of products produced by heterogeneous catalysts. Mononuclear transition metal complexes used as homogeneous catalysts may provide an answer to this and other problems associated with a heterogeneous system [2,3].

For over 50 years there has been considerable debate over the mechanism involved in Fischer-Tropsch synthesis [4,5,6], starting with the initial carbide mechanism proposed by Fischer and Tropsch themselves in 1926. Mononuclear transition metal complexes have been very helpful as models for intermediates and reaction pathways proposed in various mechanisms [7,8,9]. The synthesis and characterization of anionic and neutral formyl complexes has provided evidence for the controversial initiation step of carbon monoxide inserting into a metal hydride bond [10,11,12,13]. Rhenium formyl complexes have also been shown to react forming two other predicted intermediates such as a hydroxymethyl [14] and a methoxy complex.

The stoichiometric reaction of the zirconium complex $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{CO})_2$ with molecular hydrogen has provided some insight into the reaction pathway(s) involved in the reduction of coordinated CO on mononuclear transition metal complexes [15,16].

Within the last three years several reports of Fischer-Tropsch type synthesis involving mononuclear complexes at synthetic gas pressures under 1000 atm have been published [17,18]. These complexes were proposed to be cobalt and ruthenium carbonyl complexes and found to selectively form oxygenated products (i.e., methanol, higher 1° alcohols, formate esters, ethylene glycol, and glycerine). The ruthenium catalyst was shown to have some interesting effects on selectivity resulting from a carboxylic acid promoter [19].

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Spectroscopic Measurements of Heterogeneous Catalysts

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In trying to evaluate the performance of a catalyst in a reaction, certainly the rate and selectivity of the reaction are the most obvious and sensitive measures of that catalyst's performance. However, to improve the rate or selectivity of that reaction, or in trying to develop other catalysts, some microscopic information is needed to determine the reaction mechanism.

Techniques which look at the surface of a catalyst are needed, but observation of the catalyst under working conditions is also very desirable. No single spectroscopy exists which gives all of the needed information about the catalyst surface under reaction conditions. Thus, one is forced to use a combination of techniques to try and glean as much information as possible from the surface.

Infrared [1-9], Mössbauer [10-13], electron paramagnetic resonance [14-17], nuclear magnetic resonance [18-20], along with several other types of spectroscopy [21-23], have all been used to try and characterize heterogeneous catalysts. Also, a pair of recent books [24,25] have addressed these issues.

Tamaru feels strongly that catalytic systems must be studied under dynamic, reaction conditions [1,24]. Infrared is the technique he has chosen [1,6,8,9].

Dent and Kokes used an IR study to determine the mechanism of olefin isomerization over ZnO [4]. They demonstrated that allylic intermediates are involved. Tamaru [9] and others [7] have used dynamic IR to try and determine the mechanism of Fischer-Tropsch catalysis by supported ruthenium.

However, IR does not seem well suited to investigate molecular sieve type catalysts, and as a result methods like EPR and Mössbauer have useful applications. In a good demonstration of the application of Mössbauer spectroscopy, Boudart followed the reversible change in the oxidation state of an iron atom in a Y type zeolite, due to adsorption and desorption of gas phase molecules, and identified the Mössbauer spectrum of the adsorption complex [12].

EPR is useful in studying catalytic systems where paramagnetic species are involved. A good example is Lunsford's investigation of low spin Co(II)-methyl isocyanide complexes in Y zeolites [14]. Information is gotten on whether penta- or hexa-coordinate complexes are formed, where they form in the zeolite, and the approximate location of the unpaired electron.

Whenever possible, spectroscopic measurements of heterogeneous catalytic systems should be done in situ, or under conditions which are as similar as possible to reaction conditions. If not done, one can never be sure what the actual catalytically active species is, or how it reacts under working conditions. However, there is still much information to be gained from the use of several methods in conjunction, both before and after catalysis, on a system where in situ measurements are not yet possible.

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Catalysis by Metallocarboranes

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Alkaline degradation of the isomeric icosahedral carboranes, closo-1,2- and 1,7- $C_2B_{10}H_{12}$, to the eleven vertex nido- $C_2B_9H_{12}^-$ anions was discovered in 1964 [2]. The scope of metallocene chemistry was subsequently expanded in 1965 to include the metallocarboranes [3], polyhedral carboranes which incorporate transition metals into one or more of the vertices. The most stable and the most intensely studied [1c] metallocarboranes are those in which the metal is bonded to a capping ligand such as another nido-carborane anion or cyclopentadienide. In recent years, however, the study of metallocarboranes with potentially dissociable ligands has been the trend [1a] thus investigating the role of carborane ligands in organometallic chemistry. Research along these lines has been fruitful and has led to the discovery of catalytically active metallocarboranes [4].

The most active metallocarborane catalysts are derived from the icosahedral carborane $C_2B_{10}H_{12}$. Starting with the readily available and moderately inexpensive [5] $B_{10}H_{14}$ followed by reaction with acetonitrile or dimethylsulfide and acetylene, $C_2B_{10}H_{12}$ can be made in good yield [6]. The 1,7- and 1,12-isomers of $C_2B_{10}H_{12}$ can be obtained by thermal rearrangement of 1,2- $C_2B_{10}H_{12}$ [7]. Treatment of the icosahedral carboranes with strong base will give the eleven-particle fragments [2] having the composition $C_2B_9H_{12}^-$. The other important carborane ligands in catalytically active metallocarboranes are $C_2B_8H_{11}^-$ and $C_2B_8H_{11}^-$ which are derived from $C_2B_7H_{13}$ [2] and $C_2B_8H_{11}$ [8], respectively.

Metallocarborane catalysts are formed in high yield by the oxidative addition of a BH bond of nido- and arachno-carborane anions to coordinatively unsaturated rhodium(I) and ruthenium(II) species; this oxidative addition to unsaturated metal centers has proved to be a general reaction [4,9-15]. A dimeric rhodacarborane which represents an intermediate in this oxidative addition has been isolated and characterized crystallographically [16]. The rhodacarboranes derived from $C_2B_9H_{12}^-$ are catalysts for hydrogenation of olefins [4,11-14,16], isomerization of olefins [4,11-14,16], hydrosilation of ketones [4], and hydroformylation of alkenes [17]. Resolution of 1-phenyl-3-rhodacarborane has been followed by the use of the optically active carborane to catalyze the reduction of acetophenone with phenyldimethylsilane to give the hydrosilated product in 42% optical purity [18]. The carborane $C_2B_9H_{11}^{2-}$ has been bound to chloromethylated polystyrene and reacted with $Rh(PPh_3)_3Cl$ to give a polymer-bound catalyst [19] with distinct advantages over conventional polymer-bound catalysts. Ten [14] and eleven [13] vertex rhoda- and ruthena-carborane complexes have also been discovered to catalyze the hydrogenation of olefins. The ten and eleven vertex rhodacarboranes are less active than their twelve vertex congeners, but the ten vertex ruthenacarborane is the most active ruthenacarborane catalyst yet studied under the mild conditions employed.

The only data reported for the hydrogenation of olefins have been the initial rates and the fact that the rate is inversely proportional to the concentration of excess phosphine added [4]. This fact implies

that reversible phosphine dissociation precedes the rate determining step in the catalytic cycle. Exploitation of this has resulted in the synthesis of the most active hydrogenation catalyst yet reported [12], $\text{H}(\text{PPh}_3)\text{Rh}(\text{butenyl})\text{C}_2\text{B}_9\text{H}_{10}$, which is 30 times more active than Wilkinson's catalyst in the hydrogenation of vinyltrimethylsilane and is 4 times more active than the most active previously reported catalyst, $[\text{Ir}(\text{cod})(\text{P}^i\text{Pr}_3)(\text{py})]\text{PF}_6$ [21].

While a number of catalytic cycles based on the conventional 16 to 18 electron species can rationalize the catalytic activity of metallocarboranes, no mechanism has been posited and active species have yet to be determined. The carborane ligand is known to stabilize high oxidation states in transition metals [22], but in the rhodacarborane systems it is questionable whether a Rh(III) species is the active catalyst. The hydride on the metal center could tautomerize back to the carborane cage to form a formal Rh(I) species [23], or the Rh(III) species could heterolytically split hydrogen. The steric effects of the carborane cage may be substantial as it occupies a large portion of the catalytic surface of the metal. The carborane ligand, because of its electron deficient nature, may act as an effective trans-labilizing group [24] affecting the bonding of ligands on the opposite side of the metal.

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The removal of sulfur contaminants from fossil fuel feedstocks is important both to industry and to the environment [1]. Petroleum shortages will necessitate the refining of heavier, sulfur rich crudes which until now were not economically feasible sources of energy. Hydrodesulfurization (HDS) catalysts have been in use since the 1930's, but very little is known about the structure of the sulfided catalyst, nature of the active site, or mechanism of desulfurization of the various sulfur impurities. The majority of research in the field is on the Co-Mo/Al₂O₃ system, most commonly used in industrial applications, and has been reviewed by several authors [2-5]. Although a large body of experimental evidence exists, a consistent model of the HDS system has yet to be formed. A summary of points of general agreement, as well as models of more controversial aspects follows.

Nature of the Catalyst

The industrial catalyst is prepared by impregnation of Al₂O₃ with MoO₄²⁻ followed by calcining, impregnation with Co, and recalcining. The catalyst is activated by sulfiding. The Co is added because it greatly increases the activity of the molybdenum catalyst, with maximum promotion at ~25-40% of total metal weight. Upon interaction of Mo with the support it has been suggested that a monolayer of Mo is formed [7]. A recent spectroscopic study [8] has shown that cobalt is divided into a fraction migrating into the alumina support, as well as a fraction forming a "capping bilayer". Formation of various compounds of molybdenum and cobalt is dependent on weight percent of load, calcination temperature, pretreating condition, and method of impregnation. The lack of a consistent method of generating catalyst in the laboratory has led to conflicting reports of surface species. The active catalyst is sulfided, and there is no agreement as to the surface species present in the active catalyst. MoS₂ has been seen by electron microscopy [3], although this has been disputed [6]. The degree of Co sulfidation is also unclear.

Models for Active Site

Three theories most often considered for the structure of the active catalyst are the monolayer model, the pseudointercalation model and the synergetic model.

The monolayer model first proposed by Lipsch and Schuit [9] is now defended mainly by Massoth [10,6]. In this model sulfiding effects replacement of some terminal oxides by sulfides and removal of some to form anionic vacancies, the surface layer remaining intact. The vacancies form the active site. In the intercalation model [3,11] promoter ion intercalates at the edge of MoS₂ crystals forming reduced Mo³⁺ ions, which are exposed to the surface as the active site. Epr evidence has been cited for this theory [12,13]. The synergy-by-contact model [14,15,4] states that mixtures of cobalt and molybdenum sulfides show a considerable synergetic effect. No explanation is generally cited for this model, although a "spillover" effect has been evoked [16].

Mechanism of HDS

Early work by Amberg [17] showed that tetrahydrothiophene is not an intermediate in HDS of thiophene, leading to the widely held conclusion that C-S hydrogenolysis precedes C=C hydrogenation. However, Givens and Venuto [18] have seen dihydrobenzothiophene in HDS of benzothiophene. Most models assume adsorption at the sulfur heteroatom [9], although recent work on more condensed derivatives evokes π bonding to the catalyst [19-21].

Fundamental research on desulfurization mechanisms is attracting more attention in the literature ranging from early reports of transition metal extrusion of sulfur from organosulfur compounds [23] to activation of hydrogen by Mo-S moieties [24].

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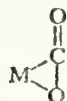
Reactions of CO₂ with Transition Metal Compounds

Winston S. Uchiyama

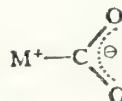
April 28, 1981

The extensive use of fossil fuels as an energy source has led to a buildup of atmospheric carbon dioxide. This buildup has caused concern among researchers due to the possible hazards of a carbon dioxide induced increase in climate, known as the greenhouse effect [1]. Studies to utilize this abundant source of carbon have become widespread and are not geared towards its catalytic regeneration to more useful forms of carbon. In order to select efficient catalytic systems, general reactivity and behavior of this molecule with transition metal compounds must be determined [2,3].

Carbon dioxide is a poor electron donor [2]. It does not readily form transition metal adducts. However, coordination to a basic, electron-rich, low-valent metal center by the carbon-oxygen π -bond, (I), or the Lewis acid site at the central carbon atom, (II) can occur [4,5].



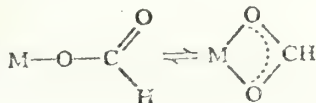
(I)



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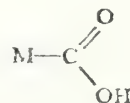
The stability of these ligands can be enhanced by a counter ion, or another ligand [6,7].

Carbon dioxide will readily insert into a metal-hydrogen bond [8]. Insertion may occur in two ways: producing a formate complex, either mono- or bi-dentate (III and IV, respectively), or a metallo-carboxylic acid (V).



(III)

(IV)



(V)

Reactions yielding the formate complex are predominant, with the formation of metallocarboxylic acids being only chemically inferred. Insertion into metal-carbon, -nitrogen, and -oxygen bonds has also been observed [9,10]. Relatively little mechanistic work has been done on these systems.

Metal complex-promoted deoxygenation and disproportionation of carbon dioxide have been investigated [11,12,13]. Complete characteri-

zation of the products has led to a better understanding of possible mechanisms. Although the reactions are noncatalytic, catalytic cycling can be inferred for some of those processes.

Recently reported catalytic reactions include the incorporation of carbon dioxide into oxiranes [14] and the oxidation of phosphines [15]. These processes are just an indication of the potential utility of CO₂ as an organic feedstock. Further understanding of its reactivity will undoubtedly produce more efficient, industrially important catalysts.

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The Syntheses and Reactivity of μ -Alkylidene Complexes

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Since the first mononuclear transition metal alkylidene complexes (metal carbenes) were reported by Fischer and Massböl in 1964 [1], hundreds of additional examples of this class of compounds have been prepared by various routes. Less is known, however, about μ -alkylidene ligands, i.e., those bridging two metal centers. During the past several years, transition metal μ -alkylidene complexes have been a growing class of compounds of considerable chemical and theoretical interest. According to theoretical considerations [2] and NMR spectroscopic evidence [3], the μ -alkylidene complexes can be formulated as dimetallacyclopropanes and appear to display high electron density at the bridging carbon.

Although most μ -alkylidene complexes contain transition metals of Fe/Co/Ni triads, compounds of this type are also known for group VI and VII transition metals. The simplest μ -alkylidene complexes, those with bridging methylene groups (μ -CH₂), have been of special interest because of their relationship to methylene groups on metal surfaces in catalytic reactions [4]. Since the first μ -methylene complex was reported in 1975 [5], this class of compounds has grown rapidly and to date examples are known for Mn [5], Rh [6], Pt [7], Os [8], Ru [9], Fe [10], and Co [11]. A compound containing a methylene ligand bridging between Ti and Al has also been reported [12].

Syntheses of μ -Alkylidene Complexes

For the preparation of μ -alkylidene complexes, direct and indirect approaches have been used [13]. One direct approach employs diazoalkane reagents [14] which are known to be outstanding carbene precursors in organic chemistry. Another direct approach uses geminal dihaloalkanes and promises to be a simple and general route to μ -alkylidene complexes [10,15].

Among the indirect approaches to μ -alkylidene complexes, two methods have attracted considerable attention. The first method involves the addition of electrophilic Fischer-type carbenes to nucleophilic and coordinatively unsaturated metal species. This provides heterobimetallic μ -alkylidene complexes [16]. The second method involves the initial insertion of alkynes into metal ligand functionalities and subsequent rearrangement of the dimetallacycles thus obtained. This method mainly leads to μ -alkylidene complexes with simple alkyl bridges [17].

Reactivity of μ -Alkylidene Complexes

Despite the intense level of recent interest in μ -alkylidene ligands in organometallic chemistry, their reaction chemistry is still largely unexplored. Substitution reactions at the methylene bridge have been reported [18]. Reactions with hydrogen and unsaturated hydrocarbons have also been investigated [10,19] due to their potential relationship to Fischer-Tropsch chemistry and to other hydrocarbon reactions catalyzed by metal complexes. Finally, the interaction of protic acids with μ -alkylidene complexes has been studied, in part, to investigate the nucleophilic activity of the bridging carbon [9,20].

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Studies of Intervalence Transfer Using Time Domain Reflectometry

Michael K. Kroeger

June 15, 1981

Intervalence transfer has widespread importance in all aspects of modern chemistry yet is still in an elementary theoretical stage. Time Domain Reflectometry (TDR) represents a novel physical technique for the study of intervalence electron transfer. The timescale for TDR is 0.5-100 nsec which brackets it between NMR and EPR. Unlike other techniques which indirectly measure intervalence transfer rates through line broadening, TDR directly observes the intervalence transfer process. In general, relaxation methods monitor the rate of equilibration after the application of a perturbation such as a pulse. TDR measures the dielectric relaxation properties of a sample which are simply the response of dipoles to an applied electric field[1-3]. The rate at which the dipoles orient with the field yields the dielectric relaxation time. The time domain indicates that the dielectric constant is observed as a function of time. Four parameters may be obtained from the TDR technique[3]: ϵ_0 , the static dielectric constant; ϵ_∞ , the optical dielectric constant; τ , the dielectric relaxation time; and σ , the DC conductivity.

For solid mixed-valence compounds the rotation of dipoles corresponds to an intervalence electron transfer between a pair of metal sites:



The dipole motion will give rise to dielectric relaxation which will be observable if it is within the TDR timescale.

Europium sulfide, Eu_3S_4 , has been shown to give rise to intervalence transfer on the Mössbauer timescale with a thermal barrier to electron transfer of 1940 cm^{-1} [4]. Our Mossbauer studies yield a thermal barrier of 2153 cm^{-1} . However, TDR results indicate a barrier of 917 cm^{-1} . It is noted that the TDR results are in better agreement with conductivity studies which report a barrier of 1290 cm^{-1} [5].

Perovskites of the general formula $\text{La}_x\text{Sr}_{1-x}\text{ZO}_3$, $Z = \text{Mn, Fe, Co, Ni}$, are presently being studied by TDR. Doping of the perovskite with strontium introduces mixed valency into the extended lattice. The parent compound LaFeO_3 exhibits no dielectric relaxation nor conductivity yet samples doped with Sr do. The sample $\text{La}_{.9}\text{Sr}_{.1}\text{FeO}_3$ has been characterized by TDR. The thermal barrier for intervalence transfer is 659 cm^{-1} and the thermal barrier for conductivity is 1430 cm^{-1} . No difference is seen between the infrared spectra of LaFeO_3 and $\text{La}_{.9}\text{Sr}_{.1}\text{FeO}_3$.

Preliminary results on $\text{La}_{.8}\text{Sr}_{.2}\text{FeO}_3$ indicate higher conductivity and lower barriers as expected. The thermal barrier for intervalence transfer is 110 cm^{-1} and the thermal barrier for conductivity is 959 cm^{-1} .

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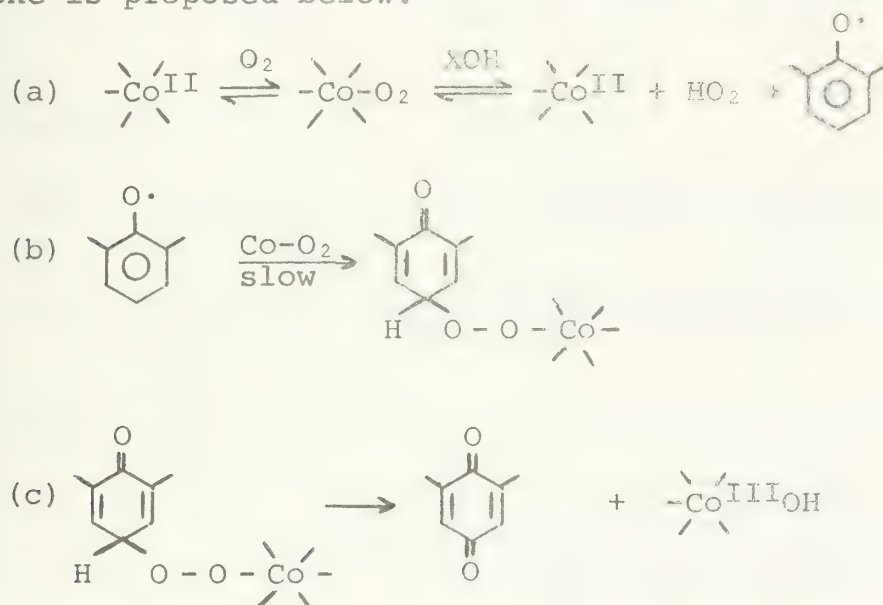
Catalytic Oxidations with Cobalt-Dioxygen Complexes

Alan Zombeck

June 15, 1981

Determining ways dioxygen can be activated by a metal center is essential for understanding both biological and commercial systems[1,2]. The goal of homogeneous catalytic oxidations is the highly selective and efficient incorporation of oxygen into organic substrates. Thus, to achieve a non-free radical concerted process, many workers have used metal-dioxygen complexes as catalysts (or as catalyst precursors) for oxidations [3-6]. However, to date there are very few oxidations which are thought to involve a true metal-dioxygen activation pathway [6].

The oxidation of hindered phenols by cobalt-dioxygen complexes may proceed via a dioxygen activation pathway since only those cobalt complexes that reversibly bind dioxygen are active catalysts in this oxidation[7-9]. A mechanistic study was conducted to determine if indeed a true dioxygen activation was operative in this case, and with this understanding, extend the potential of this catalytic system for more difficult oxidations such as olefins. From this study, the following mechanism for the oxidation of 2,6 dimethyl phenol by CoSalMDPT in benzene is proposed below:



The kinetics of the reaction, $\text{rate} = k(\text{Co})(\text{O}_2)(\text{phenol})$, support this mechanism if a steady state approximation is assumed for the phenoxyl radical concentration. The hydrogen atom abstraction, step (a), is supported by hydrogen bonding[10] and EPR[11] studies. A deuterium isotope study showed step (a) was not rate determining. Further reaction of the phenoxyl radical with a Co-O₂ species is supported by several pieces of evidence. If the phenoxyl radicals are generated simultaneously via some other reaction in the presence of a cobalt complex that does not bind O₂, NO benzoquinone is formed. Also, the EPR spectrum of a cobalt-peroxy-benzoquinone complex (similar to the one in step (b)) shows an overlapping Co-O₂ and phenoxyl radical signal, thus suggesting

an equilibrium as proposed in step (b). Catalyst deactivation studies revealed benzoquinone and water do not inhibit the reaction, but rather acids produced as oxidized side products eventually kill the catalyst. Thus, the addition of non-coordinating bases to the reaction greatly enhanced the number of turnovers.

The CoSalMDPT complex was found to be an active catalyst for the oxidation of terminal olefins to the corresponding methyl ketones and secondary alcohols. This is the first example of a cobalt complex (that binds O_2) catalyzing an oxidation to produce a unique product distribution different from typical autoxidation reactions. There is substantial evidence that indicates a unique mechanism other than a typical free radical type common to autoxidations. First, the oxidation of terminal olefins by CoSalMDPT is very solvent dependent, only ethanol is an acceptable solvent. Second, the reaction is independent of O_2 pressure. Third, no induction period is observed and the reaction is not inhibited by free radical traps. Next, styrene is easily oxidized by CoSalMDPT, whereas most autoxidation catalysts do not oxidize styrene since it does not have an allyl position available for hydroperoxide formation. Finally, typical autoxidation catalysts such as $Co(acac)_3$, do not catalyze this reaction under identical reaction conditions. A synergistic enhanced rate is observed with the addition rhodium to the CoSalMDPT catalyzed oxidation. The cobalt catalyst does not oxidize 2 hexanol, thus suggesting a mechanism where both oxidation products are derived from a common intermediate.

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University of Illinois

Inorganic Seminar Abstracts

1981-82

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Deborah Samkoff

Final Seminar

September 2, 1981

As a consequence of their relationships to transition metal-nitrosyl and transition metal-dinitrogen compounds, mononuclear transition metal arylazo compounds have been prepared and characterized in profusion during the past fifteen to twenty years[1,2]. Polynuclear transition metal compounds containing arylazo ligands, by contrast, remain relatively rare. The two structurally characterized examples have monohapto bridging arylazo ligands[3,4]; four other compounds have also been assumed to possess bridging arylazo ligands of the same structural type[5-8].

Arenediazonium salts $\text{ArN}_2^+\text{BF}_4^-$ ($\text{Ar} = p\text{-C}_6\text{H}_4\text{CH}_3$, Ph , $p\text{-C}_6\text{H}_4\text{F}$) react with $\text{H}_2\text{Os}_3(\text{CO})_{10}$ in refluxing dichloromethane to produce the compounds $\text{HOs}_3(\text{CO})_{10}(\eta^1\text{-N=N-Ar})$ (**1**). The structure of $\text{HOs}_3(\text{CO})_{10}(\eta^1\text{-N=N-}p\text{-C}_6\text{H}_4\text{CH}_3)$ has been deduced by ^{15}N NMR and confirmed by single-crystal x-ray diffraction[9].

UV ($\lambda > 297\text{ nm}$) photolyses of solutions of **1** produce the isomeric compounds $\text{HOs}_3(\text{CO})_{10}(\eta^2\text{-N=N-Ar})$ (**2**). The structure of $\text{HOs}_3(\text{CO})_{10}(\eta^2\text{-N=N-}p\text{-C}_6\text{H}_4\text{CH}_3)$ has been deduced by N NMR and the structure of $\text{HOs}_3(\text{CO})_{10}(\eta^2\text{-N=N-Ph})$ has been confirmed by single-crystal x-ray diffraction [10]. This compound is the first structurally characterized sample of a polynuclear transition metal compound containing a dihapto bridging arylazo ligand. Compounds **2** revert to **1** thermally.

Quantum yields for the photoisomerization of **1** to **2** have been estimated at 313 nm and 366 nm; they indicate that isomerization results primarily from the absorption of higher-energy light.

^{15}N NMR proved useful in the determination of the solution structures of the compounds described in this work; the technique may be generally useful for other polynuclear arylazo transition metal compounds, as well.

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REACTIONS OF MANGANESE CARBONYL RADICALS:
HYDROGEN ATOM TRANSFER AND SUBSTITUTION.

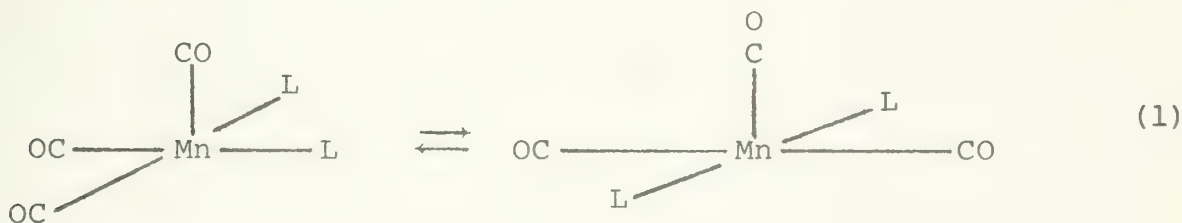
Sharon Brawner McCullen

Final Seminar

October 1, 1981

The UV-visible spectra of dinuclear metal carbonyl compounds exhibit an intense absorption ($\epsilon \sim 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) in the range of 300 to 500 nm. Gray has assigned this absorption to a $\sigma \rightarrow \sigma^*$ electron transition of the metal-metal bond. (1) Irradiation at wavelengths near the $\sigma \rightarrow \sigma^*$ transition leads to a lowering of the bond order from one to zero, resulting in homolysis of the metal-metal bond. The metal carbonyl radicals formed in this photochemical process have very short half lives, recombining at diffusion controlled rates. (2) In several cases, such as $[\eta^3\text{-C}_3\text{H}_5\text{Fe(CO)}_3]_2$, weakening of the metal-metal bond interaction as a result of steric crowding leads to the existence of an equilibrium between the dinuclear compound and its paramagnetic monomers. (3) Dimerization does not occur for $\eta^3\text{-C}_3\text{H}_5\text{Fe(CO)}_2\text{PPh}_3$ because the bulky PPh_3 ligand prevents recombination of the monomers. (4)

The extended photolysis of $\text{Mn}_2(\text{CO})_8\text{L}_2$ with L (L=phosphorus donor ligand) in hexane, with periodic removal of CO results in formation of $\text{Mn(CO)}_3\text{L}_2$. The room temperature EPR spectrum of the irradiated solution is an overlapping sextet of triplets, consistent with the assignment $\text{Mn(CO)}_3\text{L}_2$. This $17e^-$ species exhibits broad absorptions in its electronic spectrum ($\lambda_{\text{max}} = 750$ and 1120 nm) similar to that reported for Mn(CO)_5 ($\lambda_{\text{max}} = 830$ nm). (5) Molecular orbital considerations predict a square pyramidal geometry for Mn(CO)_5 , (6) therefore it is likely that $\text{Mn(CO)}_3\text{L}_2$ also has square pyramidal geometry. $\text{Mn(CO)}_3\text{L}_2$ probably undergoes rapid isomerization as shown in Eqn (1)



The reaction of $\text{Mn(CO)}_3\text{L}_2$ with CCl_4 leads to $2,4\text{-L}_2\text{-1-ClMn(CO)}_3$ as the major reaction product along with small amounts of $2,3\text{-L}_2\text{-1-ClMn(CO)}_3$ (7) suggesting that the equilibrium shown in Eqn. 1 favors trans basal positions for L in the radical. In the absence of trace amounts of oxygen the $\text{Mn(CO)}_3\text{L}_2$ radicals are stable for several weeks making it possible to study the reactions of $\text{Mn(CO)}_3\text{L}_2$ with HSnBu_3 and CO.

The reaction of $\text{Mn(CO)}_3\text{L}_2$ with HSnBu_3 results in $\text{HMn(CO)}_3\text{L}_2$ as the major reaction product based on IR and NMR data. The rate of reaction exhibits first order dependence upon the concentrations of $\text{Mn(CO)}_3\text{L}_2$ and HSnBu_3 and decreases with the increasing cone angle of L for a series of phosphorus donor ligands with similar electronic properties. (8) For ligands with similar steric requirements, increasing the π -acceptor ability of L results in a slower rate of reaction. These observations

support hydrogen atom transfer from HSnBu_3 to $\text{Mn}(\text{CO})_3\text{L}_2$ as the rate determining step in the reaction pathway.

The reaction of $\text{Mn}(\text{CO})_3\text{L}_2$ ($\text{L} = \text{P}(\text{n-Bu})_3, \text{P}(\text{i-Bu})_3$) with CO results in formation of $\text{Mn}_2(\text{CO})_8\text{L}_2$. The reaction of $\text{Mn}(\text{CO})_3[\text{P}(\text{i-Bu})_3]_2$ with CO exhibits first order dependence upon the concentrations of CO and $\text{Mn}(\text{CO})_3\text{L}_2$ and inverse dependence upon the concentration of free ligand. For a smaller ligand such as $\text{P}(\text{n-Bu})_3$ on $\text{Mn}(\text{CO})_3\text{L}_2$ reaction with CO is much faster. These observations support an associative reaction pathway for the substitution of L by CO on $\text{Mn}(\text{CO})_3\text{L}_2$.

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ISOTOPIC LABELLING AND HYDRIDE ATTACK
ON ORGANOTRIOSMIUM CLUSTER COMPOUNDS

George M. St. George

Final Seminar

October 20, 1981

The relatively new techniques of reflectance infrared-spectroscopy and high-resolution electron energy-loss spectroscopy (EELS) have provided an abundance of data pertaining to species adsorbed on metal surfaces. In several cases, however, identification of the species observed has been hindered for lack of appropriate models with which to correlate vibrational data. Metal clusters have been proposed as suitable models [1], although the transferability of vibrational data from clusters to surface species has been questioned [2].

Surface-adsorbed formate has been implicated in the surface decompositions of formic acid, as well as in the water-gas shift reaction. In order to provide chemists with a "benchmark" for identifying formate species, a full normal-coordinate analysis of the formate ligand in $\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CH})$ [3] has been performed. The complexes $\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CH})$, $\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CD})$, and $\text{HOs}_3(\text{CO})_{10}(\text{O}_2^{13}\text{CH})$ were synthesized by reaction of the appropriately-labelled formic acid with the "lightly-stabilized" complex $\text{Os}_3(\text{CO})_{10}(\text{C}_8\text{H}_{14})_2$ [4]. The good computer fit of the observed frequencies in the approximation of a free formate ligand indicates that metal involvement in the normal coordinates is negligible. The abnormally high C-H stretching force constant and $^1\text{J}_{\text{CH}}$ values for the complex have been attributed to significant covalency in the metal-ligand bonding. Comparison with the observed frequencies for formate adsorbed on Cu(100) [5a] and Ag(110) [5b] supports the applicability of the complex as a reference for surface formate.

The nature of the species occurring from adsorption of C_2H_2 and C_2H_4 on Pt(111) [6] has been hotly debated by Ibach, Demuth, and Somorjai [7]. In an attempt to clarify the matter, vibrational studies have been undertaken on the complexes $\text{HOs}_3(\text{CO})_{10}(\text{CHCH}_2)$ and $\text{H}_2\text{Os}_3(\text{CO})_9(\text{CCH}_2)$ [8]. The vinyl complexes were prepared by insertion of C_2H_2 or C_2D_2 into $\text{H}_2\text{Os}_3(\text{CO})_{10}$ or $\text{D}_2\text{Os}_3(\text{CO})_{10}$. The insertions gave rigorously cis-labelled vinyl ligands. Trans-labelled species were made by base-catalyzed isomerization. The vinylidene complexes were synthesized by pyrolysis of the vinyl complexes. A poor computer fit to the observed frequencies in both types of complex has been interpreted as implying significant metal involvement in "ligand" normal coordinates. A study of the more complete model Os_3CCH_2 is underway. Comparison of the observed infrared frequencies of the clusters with EELS data from adsorbed C_2H_2 and C_2H_4 on Pt(111) [6] strongly implicates vinylidene species as the predominant form of annealed $\text{C}_2\text{H}_2/\text{Pt}(111)$ and implicates the absence of vinyl species in $\text{C}_2\text{H}_4/\text{Pt}(111)$.

The observed base-catalyzed isomerization of the labelled vinyl complexes, together with the previous report of a phosphine adduct of $\text{HOs}_3(\text{CO})_{10}(\text{CHCH}_2)$ [9], prompted the reaction of LiHBEt_3

with $\text{HOs}_3(\text{CO})_{10}(\text{CHCH}_2)$ to give the ethylidene complex $\text{HOs}_3(\text{CO})_{10}(\text{CHCH}_3)^-$, isolated as tetraalkylammonium salts. Hydride attack at the β -carbon of $\text{H}_2\text{Os}_3(\text{CO})_9(\text{CCH}_2)$ gives the ethylidyne complex $\text{H}_2\text{Os}_3(\text{CO})_9(\text{CCH}_3)^-$, similarly isolated. Hydride also attacks the α -carbon of the μ_2 -carbyne complex $\text{HOs}_3(\text{CO})_{10}(\text{COCH}_3)$ to give the methoxycarbene complex $\text{HOs}_3(\text{CO})_{10}(\text{CHOCH}_3)^-$. It was hoped that protonation of this complex would give the methyne complex $\text{HOs}_3(\text{CO})_{10}(\text{CH})$. The reactivity of the product, however, indicates that CO insertion has occurred to give the ketenyl complex $\text{HOs}_3(\text{CO})_9(\text{CHCO})$.

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RECENT DEVELOPMENTS IN TECHNETIUM COORDINATION CHEMISTRY AND ITS MEDICAL APPLICATION

Joshua Telser

Literature Seminar

November 10, 1981

Technetium occupies a unique place in chemistry as the first non-naturally occurring element prepared by nuclear synthesis. Its absence from nature results from the instability of odd atomic numbered elements [1]. Technetium has a number of isotopes of which ^{99}Tc is the most important. This isotope has a ground state with a half-life of 2.15×10^5 y and a metastable state, $^{99\text{m}}\text{Tc}$, with a half-life of 6 h. $^{99\text{m}}\text{Tc}$ is widely used as a radiopharmaceutical for diagnostic organ imaging [2]. Technetium is obtained on a fairly large scale as a by-product of nuclear fission or by neutron bombardment of ^{98}Mo and can be safely used in chemical research using appropriate precautions [3,4].

Technetium chemically resembles the other group VIIb elements, manganese and particularly rhenium. Technetium exhibits a wide range of oxidation states from (-I) to (VII) with (IV) and (VII) the most common. It forms a number of simple oxides, e.g., TcO_2 , Tc_2O_7 ; sulfides, halides, e.g., TcCl_4 , TeF_6^{-2} and oxo halides such as TcOBr_3 and TcO_3F [3-5]. Tc_2O_7 dissolves in water to give pertechnic acid, HTcO_4 . The pertechnate ion is very stable and is the starting point for most technetium coordination compounds. Low oxidation state complexes can be prepared using phosphine, arsine and phosphonite ligands, including an interesting seven-coordinate species $[\text{TcCl}_3\text{CO}(\text{PMe}_2\text{Ph})_3] \cdot \text{EtOH}$ having capped octahedral symmetry [6]. Another seven coordinate complex has been synthesized by $\text{Sn}(\text{II})$ reduction of TcO_4^- in dimethylglyoxime [7]. This complex is of interest since similar procedures are used to prepare technetium radiopharmaceuticals, whose chemical nature are often not well understood. Other high coordination number complexes have been synthesized with cyanide and thiocyanate ligands [8]. An eight coordinate complex has been prepared by oxidative addition of Cl_2 to $[\text{Tc}(\text{diars})_2\text{Cl}_2]^+$ [9]. This type of oxidative addition is unusual and demonstrates the wide possibilities in technetium coordination chemistry. A $\text{Tc}(\text{V})$ compound containing the ligand hydrotris(1-pyrazolyl)borate has been synthesized from aqueous solution [10]. This is of potential importance in preparing lipophilic Tc-labeled radiopharmaceuticals from technetate solutions. A large series of $\text{Tc}(\text{V})$ compounds of general form $[\text{TcOY}_4]$ where $\text{Y}_4 = \text{X}_4$, S_4 , S_2O_2 and S_2N_2 containing ligands have been synthesized and well characterized by spectroscopic methods [11-13]. One point of interest is that in the attempted synthesis of a technetium thioglycolate complex, a mercaptothioacetate complex was obtained instead [11]. This demonstrates that technetium radiopharmaceuticals prepared by reduction of TcO_4^- in the presence of a ligand may not give the expected complex. Technetium phosphate complexes have been prepared and one characterized by x-ray crystallography [14]. The complex consists of infinite polymeric chains of phosphate bridged technetium atoms. Complexes such as this are thought to bind to Ca^{+2} sites in bone via uncoordinated phosphates [15].

Diagnostic organ imaging, for which technetium complexes are used, consists of the intravenous administration of a radiopharmaceutical which becomes distributed throughout the body tissues in a pattern

characteristic of the complex [2]. The distribution is monitored by a scintillation camera which gives a two-dimensional picture showing diseased areas. A large number of isotopes are used; however, ^{99m}Tc has nearly ideal chemical and physical properties as well as ready availability. Many technetium complexes are used for imaging a wide variety of body tissues and new ones are constantly being developed [16,17]. Concomittant with this revolution in medical technology, great advances have been made in recent years in technetium coordination chemistry. However, much further investigation into technetium chemistry is needed in order to better understand the action of existing Tc-labeled radiopharmaceuticals and to design new ones.

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Flash Photolysis Studies of Dinuclear Transition Metal Carbonyl Compounds

Robert J. Olsen

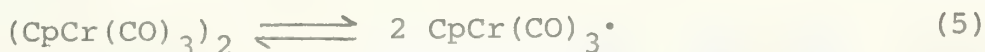
December 10, 1981

Dinuclear transition metal carbonyl compounds possess an intense absorption ($\epsilon \sim 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) in the 300-500 nm region of their UV-VIS spectra. Gray and co-workers determined that this absorption is polarized along the metal-metal axis and assigned this band to the $\sigma \rightarrow \sigma^*$ transition [1]. Irradiation at wavelengths in the $\sigma \rightarrow \sigma^*$ region results in a change in the metal-metal bond order from one to zero, generating radicals in solution. Kidd and Brown studied the photochemical reaction of $\text{Mn}_2(\text{CO})_{10}$ with phosphine, L, and found $\text{Mn}_2(\text{CO})_8\text{L}_2$ to be the major product [2]. Since the quantum yield of disappearance, Φ_d , of the reaction is independent of the concentration and the nature of the phosphine, they proposed that substitution most likely occurs by dissociative loss of CO from $\text{Mn}(\text{CO})_5\cdot$, followed by rapid reaction with phosphine (Steps 2 and 3):



Other reactions, including thermal substitution of phosphine onto transition metal hydrides [3,4] and the thermal decomposition of $\text{HCo}(\text{CO})_4$ to $\text{Co}_2(\text{CO})_8$ [5], are also thought to proceed via reactive unsubstituted radical centers. Brown and co-workers have studied the photochemical reaction of $\text{Mn}_2(\text{CO})_8(\text{P}(\text{OC}_2\text{H}_5)_3)_2$ with $\text{P}(\text{n-C}_4\text{H}_9)_3$ [2]. $\text{Mn}_2(\text{CO})_8(\text{P}(\text{n-C}_4\text{H}_9)_3)_2$ was the major product. The Φ_d increased with increasing concentrations of $\text{P}(\text{n-C}_4\text{H}_9)_3$. Associative attack of $\text{P}(\text{n-C}_4\text{H}_9)_3$ on the monosubstituted radical, $\text{Mn}(\text{CO})_4(\text{P}(\text{OC}_2\text{H}_5)_3)\cdot$, was proposed as an intermediate step in the reaction. Hence, the mechanism of substitution onto a transition metal carbonyl radical may vary, depending upon the extent of substitution and/or which ligand is being substituted, CO or L.

Steric factors influence the strength of the metal-metal bond in transition metal carbonyl dimers and in the extreme cases prevent recombination of the radical species. Cotton and co-workers have found $(\text{CpCr}(\text{CO})_3)_2$ in solution to be in equilibrium with its corresponding monomer [6]:



The following year Muetterties reported that $((\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_2\text{L})_2$ dissociated in solution to generate $(\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_2\text{L}\cdot$ [7]. In the case where L is the bulky phosphine, PPh_3 , there is no evidence for the dinuclear compound in solution. Most recently, Brown and co-workers have reported the synthesis of several persistent disubstituted manganese (0) radicals, $\text{Mn}(\text{CO})_3\text{L}_2\cdot$ ($\text{L} = \text{P}(\text{n-C}_4\text{H}_9)_3$, $\text{P}(\text{i-C}_4\text{H}_9)_3$, $\text{P}(\text{OC}_2\text{H}_5)_3$, $\text{P}(\text{i-C}_3\text{H}_7)_3$) [8,9].

Flash photolysis has been used to investigate the substitution and steric properties of unsubstituted and monosubstituted transition metal radicals. This technique involves imparting a short pulse of light (~ 150 μsec) onto a solution containing a dinuclear compound, and then indirectly monitoring the radicals generated by the pulse via a detection system focused on the $\sigma \rightarrow \sigma^*$ transition of the dinuclear compound. The radical species do not absorb in this region. Flash photolysis has been performed on hexane solutions of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$. Under 1 atm CO pressure, the dinuclear species absorbance returns to the original value in accordance with a simple bimolecular rate law. Hence, bimolecular recombination of the $\text{M}(\text{CO})_5\cdot$ radicals is most likely the major process occurring in the solution. The unsubstituted radical recombination rate is near the diffusion-controlled limit. Without an initial CO concentration, an entirely different result is obtained. Intermediates are formed which are more strongly absorbing in the 350-500 nm region than the $\text{M}_2(\text{CO})_{10}$ compounds. $\text{M}_2(\text{CO})_8$ and $\text{M}_2(\text{CO})_9$ are proposed as these intermediates. Their formation would result from the thermal loss of CO from $\text{M}(\text{CO})_5\cdot$ to generate $\text{M}(\text{CO})_4\cdot$, which would either react with itself or $\text{M}(\text{CO})_5\cdot$ to form $\text{M}_2(\text{CO})_8$ and $\text{M}_2(\text{CO})_9$, respectively. Computer modeling of the kinetics supports this scheme. Flash photolysis experiments were performed on the disubstituted dinuclear compounds, $\text{Mn}_2(\text{CO})_8\text{L}_2$ ($\text{L} = \text{P}(\text{CH}_3)_3$, $\text{P}(\text{n-C}_4\text{H}_9)_3$, $\text{P}(\text{i-C}_4\text{H}_9)_3$, $\text{P}(\text{i-C}_3\text{H}_7)_3$, $\text{P}(\text{OPh})_3$, PPh_3). With an initial CO concentration, the change in absorbance immediately after flashing followed second order kinetics, indicating sample recombination of the radicals was the major process occurring. The rate of recombination was found to decrease with increasing size of the phosphine ligand. The electronic properties of the phosphine ligand appear to have a negligible effect on the rate of radical recombination. Computer modeling enabled an upper limit to be placed on the rate of phosphine dissociation from $\text{Mn}(\text{CO})_4\text{L}\cdot$. Without an initial CO concentration, a strongly absorbing intermediate is formed upon photolyzing $\text{Mn}_2(\text{CO})_8\text{L}_2$ (analogous to $\text{M}_2(\text{CO})_{10}$), even with an initial L concentration. This suggests that CO dissociates from $\text{Mn}(\text{CO})_4\text{L}\cdot$.

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MAIN GROUP CLUSTERS OF GROUPS 4, 5, AND 6A

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Literature Seminar

March 4, 1982

Structurally, clusters may be viewed as intermediate forms between bulk elements and their isolated atoms or ions. Because of the great degree of direct atomic bonding, they create polycyclic systems. Clusters are found of most all the elements and may be neutral, cationic, or anionic [1]. The neutral clusters may be a link between the structures of solid materials and known isolated molecules, while the anionic and cationic clusters can be viewed as "frozen" models for the stepwise oxidation and reduction of the elements [2].

These main group clusters may be separated conveniently into two categories, homonuclear and heteronuclear systems. Both categories are well known with the Te_4^{2+} ion first synthesized by Klaproth in 1798 [3] and P_4S_3 (the common ingredient in "strike anywhere" match heads) discovered by Lemoine in 1864 [4]. Since that time many more clusters have been prepared and characterized using a variety of synthetic and physical techniques. Most recently, main group clusters have been used as ligands for various transition metals and exhibit several modes of coordination [5].

Early work by Zintl and co-workers [6,7] was the first to accurately characterize a number of homoatomic polyanions. Their work included characterization of polyanions of tin, lead, arsenic, antimony, bismuth, sulfur, selenium, and tellurium. Using potentiometric titrations of sodium-liquid ammonia solutions and extractions of alkali metal alloys of post-transition elements, both cluster size and charge were determined. No crystalline solids could be isolated, however, because the ammoniated sodium cation loses ammonia at room temperature, leading to polyanion decomposition.

The smallest homonuclear cluster system is one containing four atoms. For groups 4, 5, and 6A, the P_4 and Si_4^{4-} clusters [8] exist as tetrahedra, while Si_4^{6-} [9] assumes a butterfly configuration. The isoelectronic species Bi_5^{3+} [10], Pb_5^{2-} and Sn_5^{2-} [11] represent pentanuclear clusters and provide an insight into the synthesis of many larger clusters of Groups 4, 5, and 6A. The trigonal prismatic structure of Te_6^{4+} [12] represents a breakdown in rationalizing bonding with two-center, electron pair bonds. Starting with an A_4 tetrahedral core, the isostructural and isoelectronic clusters As_7^{3-} [13], Sb_7^{3-} [14], and P_7^{3-} [15] can be assembled by the addition of an A^- unit to each of three edges. The P_7^{3-} case exhibits an exchange process giving rise to equivalence of all phosphorus in the ^{31}P NMR at 80°C. The nonanuclear clusters Bi_9^{5+} [16], Sn_9^{4-} [17], Ge_9^{2-} , and Ge_9^{4-} [18] point out the close relationship between the tricapped trigonal prism and the capped square antiprism. The structure of the Sn_9^{4-} cluster in solution has been studied by ^{119}Sn NMR [19] and show rapid intramolecular exchange similar to that seen in the P_7^{3-} molecule. In higher nuclearity clusters, P_{10}^{6-} [20] may be viewed as a derivative of the P_4 tetrahedron, isoelectronic clusters

As_{11}^{3-} [21] and P_{11}^{3-} [22] although complicated at first appearance, may be broken down into derivatives of smaller simpler clusters. However, the Se_{10}^{2+} [23] species fails to fit into any logical pattern.

Heteronuclear clusters can be visualized as derivatives of homonuclear species by addition or substitution of atoms or iso-electronic units to these homonuclear clusters. Examples of this relationship are the P_4 to $\alpha\text{-P}_3\text{S}_1$, Te_4^{4+} to As_4Se_4 , S_8 to S_4N_4 [24] and As_7^{3-} to As_3Se_4^+ [25] pairs.

A primary goal of main group cluster chemistry of groups 4, 5, and 6A is the development of a scheme to interpret the bonding and predict the structure of these clusters. Lauher's molecular orbital treatment of transition metal clusters [26] is reasonably successful when applied to these main group clusters, for it deals with a localized bonding approach. The optimized syntheses of new and existing clusters are continually being sought. With the synthesis of substituted clusters and their use as ligands for transition metals, relatively new areas of chemistry are being explored including the use of chiral cluster ligands in selective synthesis [1].

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STRUCTURAL FEATURES OF ORGANOACTINIDE COMPOUNDS

John J. Gawienowski

Literature Seminar

March 11, 1982

Many organoactinide compounds have been synthesized, most within the past 15 years[1]. These compounds frequently have very high formal coordination numbers and cannot be characterized by electron counting procedures similar to the 18 electron rule of the transition element organometallics. For instance, $U(\eta^5-Cp)_4$ would have a formal coordination number of 12 and a formal electron count of $26 e^-$. Raymond and Eigenbrot have recently proposed a formalism, based on structural data, that offers the first systematic explanation for the bonding of the organoactinides[2].

Although Uranium and Thorium are the only naturally occurring actinides and dominate organoactinide chemistry, representative compounds of all elements between Actinium ($Z=89$) and Californium ($Z=98$) are known[3]. Ionic radii are large (1.03\AA for 6-coordinate U^{+4} compared to 0.85\AA for Hf^{+4} [4]) which allow for the high coordination numbers. In contrast with the lanthanides, which are mostly limited to the +3 oxidation state, the actinides display a variety of oxidation states. The organometallic chemistry of the early actinides is often compared to that of the group 4 transition elements rather than to that of the lanthanides [1a, 1b, 5].

Technologically encouraging catalytic activity has been observed by a SNAM PROGETTI group using Uranium π -allyl complexes as stereo-specific butadiene catalysts[6]. Yields $>98.5\%$ cis isomer are observed. Other catalytic activity can be envisioned involving the high oxygen affinity of the actinides, such as the activation of carbon monoxide or related compounds that Marks has been investigating[7].

Classes of Organoactinide Compounds

Biscyclooctatetrane compounds of the actinides have been actively studied since Streitwieser reported synthesis of uranocene in 1968[8]. Initial reasoning for synthesis of this compound was based on the possible overlap of the LUMO of the cyclooctatetrane dianion with 5f-orbitals of the same symmetry. A subsequent SCF-X α MO study indicated that 5f-orbital overlap is indeed important, but also indicated important 6d-orbital overlap of equal or greater magnitude[9]. In a recent communication Streitwieser reports synthesis of bis(bicyclooctatetraenyl)diuranium or "biuranocene"[10]. Interestingly, the linked cyclooctatetrane rings are twisted with respect to each other, resulting in close contact between the α hydrogens and both uranium atoms. This compound indicates mixed valence and mixed central metal compounds may be synthetically feasible.

The largest class of organoactinides is the cyclopentadienyls. Compounds of the general formulas $M(Cp)_4$, $M(Cp)_3$, $M(Cp)_3X$, $M(Cp)_2X_2$, $M(Cp)_2X$ and $M(Cp)X_3$ are known ($M=U$ or Th , X =halide, alkoxy, alkyl)[11]. These compounds appear to have more covalent chemical behavior than the corresponding lanthanides. Compounds analogous to the $M(Cp)_2X_2$

actinides also exist for the group 4 transition elements (M=Ti, Zr or Hf). Comparison of these compounds by photoelectron spectroscopy reveals a striking degree of similarity, indicating that the mode of bonding is essentially similar[11].

Structural Characteristics

Raymond and Eigenbrot have proposed a formalism based on the extensive structural data now available[2]. Within each class of f-element organometallics, two generalizations are maintained. First, the geometries of ionic compounds tend to be irregular and depend on the steric bulk, number, and charge of ligands. Coordination number observed will be the balance of ionic attractive forces and nonbonding repulsions. Secondly, bond lengths for a series of structurally similar compounds will systematically follow their "ion size" and coordination number; that is, ionic radii can be used to predict bond lengths. Predominantly covalent interactions should depart from these predictions.

Using Pauling's radius ratio approach[12] and Shannon's table of ionic radii[4], Raymond and Eigenbrot observed that the difference between the metal to carbon bond lengths and the ionic radius of the metal was essentially constant for f-element cyclopentadienyl and cyclooctatetranyl structures. In other words, the cyclopentadienyl and cyclooctatetranyl ligands have a constant ionic radius. When this system was applied to the d-block metallocenes they observed no single ionic radius for the cyclopentadienyl ligand. Thus, they conclude that the f-block organometallics have basically ionic metal-ligand interactions while the d-block metallocenes have basically covalent metal-ligand interactions.

Recently, Day et al. pointed out that $\{U[\eta^5-(CH_3)_5C_5]\mu-Cl\}_3$ is not well described by this formalism[13]. Comparison of this species with other known bridged trimers does not give a consistent value for the ionic radius of the pentamethylcyclopentadienyl ligand. However, this may be due to steric interactions between the more restricted ligands in the trimer. In any case, the proposed formalism does give a systematic characterization for the mode of bonding in organoactinide compounds which has been lacking until now. Still to be explained are the observed chemical and spectroscopic properties which indicate a larger degree of covalency than the formalism would allow.

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I. Introduction

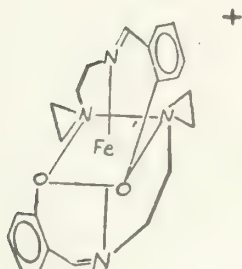
Spin-crossover complexes possess two nearly degenerate electronic states of different spin multiplicity. The aim of most investigators has been to assess ligand-field strength and substituent effects on the position of the resulting high-spin ("HS") \rightleftharpoons low-spin ("LS") "spin equilibrium." In the course of these studies, conducted over fifty years' time [1], many "curiosities" have perplexed chemists: incomplete transitions; abrupt transitions; remarkable influence of solvation or lattice counter ion [2], dependence on sample preparation; effects of grinding and doping solids [3a,c]. Non-linear plots of $\log K$ vs. $1/T$ and observations of thermal hysteresis demonstrate that kinetic influences can be as important as thermodynamic factors. In recent years efforts have intensified to explain these curiosities in terms of the theories of cooperative phase transitions, such as nucleation and growth [3], various domain models [4], or in the context of electron-phonon interactions (vibronic coupling) [5].

In spite of their non-equilibrium properties, spin-crossover coordination complexes can potentially provide valuable information about the fundamental aspects of electron transfer ("ET") processes; the "spin-flipping" phenomenon corresponds to transfer of electron(s) between thermally populated t_{2g} and e_g (*) d-orbitals with concomitant dimensional changes within the metal ion coordination sphere. For a number of spin-crossover complexes in fluid solutions near room temperature, intramolecular ET rate constants in the range $\sim 10^6 - 10^9 \text{ s}^{-1}$ have been measured directly by ultrasonic or temperature-jump techniques [6]. However, for solids no direct methods are available and one must estimate the rates by spectroscopic techniques. Almost all known spin-crossover solids observed by any such technique show discrete HS and LS resonances at all temperatures (rates considerably slower than $\sim 10^7 \text{ s}^{-1}$); the most notable exceptions are the highly covalent ferric (tris)dithiocarbamates [7], which exhibit a single population-weighted average Mössbauer quadrupole doublet at all temperatures (rates faster than $\sim 10^8 \text{ s}^{-1}$). The intent of the current investigation is to examine over a broad temperature range the electron dynamics of spin-crossover solids for which the spin-flipping occurs at an intermediate rate. An attempt is made to characterize the relationship between this intramolecular rate process and the cooperative spin-crossover phase transition.

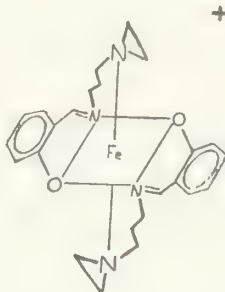
II. Characterization of New Ferric Schiff Base Complexes

The present studies focus upon the new N_4O_2 ferric complexes of the Schiff bases derived from salicylaldehyde and N-(aminoalkyl)-aziridines. Microcrystalline solids are prepared by Schiff base formation in a methanolic solution containing either $FeCl_3 \cdot 6H_2O$ /excess $NaClO_4 \cdot H_2O$ or $Fe(ClO_4)_2 \cdot 6H_2O$. The perchlorate salts of

these bis(tridentate) complexes are identified as $[\text{FeE}]\text{ClO}_4$ and $[\text{FeP}]\text{ClO}_4$, respectively, for the cases of two-carbon ("E" = ethylene) and three-carbon ("P" = propylene) bridges between the imine and tertiary amine nitrogen donors. The existence of $[\text{FeE}]^+$ and $[\text{FeP}]^+$



I



II

as meridonal (cis-oxygen, I) and centrosymmetric facial (all trans, II) geometric isomers, respectively, may be inferred from pronounced differences in the LS g-tensors and quadrupole splittings and from the results of x-ray crystallographic studies of Schiff base complexes of structurally similar tridentate [8a] and hexadentate ligands [8b].

Both $[\text{FeE}]\text{ClO}_4$ and $[\text{FeP}]\text{ClO}_4$ exhibit spin-crossover behavior in the solid state, as demonstrated by their variable-temperature magnetic moments and EPR and Mössbauer spectroscopies. $[\text{FeE}]\text{ClO}_4$ is a "high-plateauing" compound that varies from totally HS at room temperature to ~80% HS at 4.2 K; discrete LS and HS Mössbauer doublets are observed, with only the relative areas changing significantly with temperature. The magnetic data for $[\text{FeP}]\text{ClO}_4$ reveals a gradual but complete transition from ~55% HS to entirely LS over the range 300-4.2 K; a single average quadrupole doublet is seen over this entire temperature range, characterizing $[\text{FeP}]\text{ClO}_4$ as the first N_4O_2 complex shown to have an ET rate constant greater than $\sim 10^8 \text{ s}^{-1}$ [9]. Furthermore, the variable-temperature Mössbauer spectra for $[\text{FeP}]\text{ClO}_4$ exhibit (1) a very pronounced variation in the average ΔE_0 value (2.4 mm/s at 4.2 K; 1.1 mm/s at 300 K), and (2) a maximum in linewidths at ~240 K. The latter observation is interpreted as a possible clue that the spin-flipping rate is just barely faster than the characteristic Mössbauer frequency [10].

III. Properties of "Perturbed" Samples of $[\text{FeP}]\text{ClO}_4$

Preliminary Mössbauer experiments [11] for a sample of natural isotopic composition had intimated previously that, among all spin-crossover materials, $[\text{FeP}]\text{ClO}_4$ uniquely undergoes the spin state interconversion at an intermediate rate, giving rise to line broadening and subsequent coalescence of LS and HS doublets as the temperature is increased over the range of 90-293 K. It

appeared possible to extract ET rate constants from each Mössbauer spectrum by least-squares fitting to a suitable LS \rightleftharpoons HS cross-relaxation model. The Arrhenius plots resulting from such analyses of the early Mössbauer spectra gave hints of an ET mechanism involving quantum-mechanical tunneling, as proposed quite recently in a theoretical paper by Jortner and co-workers [12]. However, the poor counting statistics offered by $[\text{FeP}]\text{ClO}_4$ samples of natural isotopic composition greatly limits the reliability of the Mössbauer kinetic parameters; such was the motivation for preparing ^{57}Fe -enriched $[\text{FeP}]\text{ClO}_4$.

In an attempt to understand the reasons for the disturbing contradiction between the Mössbauer results of our earlier investigation and those described in Section II, several "perturbed" samples, all originating from the same ^{57}Fe -enriched material characterized by "fast" ($\geq 10^8 \text{ s}^{-1}$) ET rates over the entire range 4.2-310 K, have been prepared:

1. A dichloromethane-solvated compound obtained by recrystallization of a portion of the "unperturbed" $[\text{}^{57}\text{FeP}]\text{ClO}_4$ from a 3:1 $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{12}$ mixture.
2. A sample resulting from vacuum desiccation of the solvate at 56°C .
3. A hand-ground (by mortar and pestle) portion of the visibly microcrystalline unperturbed complex.
4. The products of two successive recrystallizations from $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{12}$ of the hand-ground material.
5. The microcrystalline members of an isomorphous series of cobalt-doped complexes, $[(\text{Fe}_x\text{Co}_{1-x})\text{P}]\text{ClO}_4$.
6. An iron-deficient, amorphous film isolated from a $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{12}$ solution made from the evaporated filtrate of the mother liquor.

These "perturbed" materials have been characterized by their infrared, EPR and Mössbauer spectra and by their magnetic moments and x-ray powder diffraction patterns. It is apparent that for all except the highly crystalline CH_2Cl_2 solvate, the mean rate of intramolecular electron transfer is considerably slower than that for unperturbed $[\text{FeP}]\text{ClO}_4$. These results are in keeping with the already well-established extreme sensitivity of spin-crossover complexes to their solid state environs. It is postulated that electron-phonon interactions, lattice defects or strain cause deviations from equilibrium behavior not only for a crystallite undergoing a static HS \leftrightarrow LS phase transition, but also for individual molecules undergoing a quasi-dynamic HS \rightleftharpoons LS inter-conversion.

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9. [FeP]ClO<sub>4</sub> is also the first reported spin-crossover N<sub>4</sub>O<sub>2</sub> complex in which the nitrogen donors are separated by three carbon atoms rather than two.
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# RECENT DEVELOPMENTS IN PHOTOCHEMICAL H<sub>2</sub> PRODUCTION FROM AQUEOUS SOLUTIONS OF TRANSITION METAL IONS

Kenneth Rahmoeller

Literature Seminar

March 25, 1982

Current sources of useful energy are becoming increasingly unreliable. Many systems have been proposed to convert available energy to a more practical form. One promising choice is the conversion of sunlight to a storable form of chemical energy such as H<sub>2</sub>.

For many years several aqueous metal solutions (Fe<sup>2+</sup>, Cr<sup>2+</sup>, Ce<sup>3+</sup>, Cu<sup>+</sup>) have been known to produce hydrogen from water upon irradiation by light [1]. In their present state, however, none of these systems are adequate since all require the use of ultraviolet light which does not penetrate the earth's atmosphere. In addition, once oxidized, the majority of metal ions become incapable of further activity until they are reduced (chemically or electrochemically). Recently, research in this area has increased, with a particular emphasis towards understanding the mechanisms of these potential hydrogen producing catalysts and thus finding ways to modify the conditions needed for efficient absorption of solar radiation. These systems may be broken down into several classes: solvated electron formation, production of metal hydrides, and polynuclear metal systems.

Chromium(II) has been found to produce H<sub>2</sub> and Cr<sup>3+</sup> when irradiated with UV light. Ryan and Espenson [2] demonstrated that a solvated electron was generated during the photo-induced step which quickly reacted with H<sup>+</sup>(H<sub>2</sub>O) to give a hydrogen atom. Subsequent reaction with Cr<sup>2+</sup> yields CrH<sup>2+</sup> which breaks down in acid to yield H<sub>2</sub>. Unfortunately, this process neither uses available sunlight nor allows the Cr<sup>2+</sup> to be regenerated. Hence, this system is only of interest mechanistically.

Sakharovskii [3-5] determined that Co(CN)<sub>5</sub><sup>3-</sup> will also produce H<sub>2</sub> in UV light. A probable mechanism was proposed involving formation of a hydride, but very little is known about this reaction. An encouraging discovery was that the resulting Co(III) product could also be reconverted to Co(CN)<sub>5</sub><sup>3-</sup> upon irradiation by UV light, although the results are far from clear [6].

A solution of HCl may be converted to H<sub>2</sub> and Cl<sub>2</sub> when irradiated with 254 nm light in the presence of IrCl<sub>6</sub><sup>3-</sup> [7]. This is an example of a true cyclic process. While there is disagreement concerning the mechanism [8], the results are promising. Gray suggests that the use of IrBr<sub>6</sub><sup>3-</sup> might allow the use of longer wavelengths during irradiation.

Some polynuclear metal systems may be the best answer to the photochemical production of hydrogen [9]. Their ability to maintain several different oxidation states and their low-lying excited states may allow a higher quantum yield of hydrogen. Mo<sub>2</sub>Cl<sub>8</sub><sup>4-</sup>, which supposedly generates H<sub>2</sub> by a ligand to metal charge transfer



(LMCT) transition [10], has stirred interest since the LMCT transition usually requires less energy than a transition involving the production of a solvated electron (CTTS).

Polymolybdates demonstrate a photogalvanic effect [11-13]. Upon irradiation by UV light,  $[\text{NH}_3\text{Pr}]_6[\text{Mo}_7\text{O}_{24}]$  is converted to a mixed oxidation state containing one Mo(V) center. The resulting half-cell between this species and  $\text{Mo}_7\text{O}_{24}^{6-}$  has a large enough potential to reduce  $\text{H}^+$  at a platinum electrode. Polytungstates have been found to exhibit this same effect [14], with the added benefit that the required energy of irradiation is less than for the polymolybdates.

While it must be pointed out that none of these systems are as yet workable, progress is being made. The wavelengths of light required still need to be increased to match the available solar spectrum, and the quantum yields obtained so far must be increased. By using different ligands and/or modifying the metal centers, truly photocatalytic splitting of water should become possible.

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Ruthenium and rhodium exchanged zeolites are becoming increasingly important as catalysts for a variety of chemical reactions, such as the Fischer-Tropsch reaction, [1] the water-gas shift reaction, [2] the reduction of  $\text{NO}_x$  to  $\text{N}_2$ , [3] and the dimerization of polyenes. [4] Transition metal complexes in zeolites are of interest as possible catalytic intermediates in these reactions. [5] It may also be possible to relate these complexes to intermediate species in homogeneous catalysis. [6]

Zeolites are aluminosilicate framework molecules, consisting of  $\text{AlO}_4^-$  and  $\text{SiO}_4$  tetrahedra linked together through common oxygen atoms. These zeolites have a three-dimensional network of channels or linked cavities in which molecules may be adsorbed. [7-9] Zeolite Y, a synthetic analogue of faujasite, is often used in catalysis because of its large pore size compared to other zeolites.

Transition metal ions or cationic complexes may be exchanged into zeolites. The stability of these complexes in the zeolite may be considerably altered with respect to their stability in solution. [10] The cations can be located at defined sites within the framework. [11] The geometries of the complexes are often governed by the zeolite morphology. [12]

EPR spectroscopy has been used to study transition metal complexes in zeolites, particularly those of the first transition series. [10,13] More recently, complexes of ruthenium and rhodium have been studied with EPR.

Rhodium zeolites are prepared by the ion exchange of  $[\text{Rh}(\text{NH}_3)_5\text{Cl}]^{2+}$  onto NaY zeolite. Samples are activated at high temperatures. This treatment completely decomposes the chloro-ammine complex. After treatment, paramagnetic species are formed which have been observed with EPR spectroscopy. Naccache and co-workers assign the paramagnetic species to rhodium(II) ions located at site I, coordinated octahedrally to six oxide framework ions. [14] Atanasova and co-workers propose the formation of paramagnetic ion pairs of rhodium. [15] A new paramagnetic species is formed upon adsorption of CO on the activated rhodium zeolite. This species is thought to be a mononuclear, monocarbonyl rhodium(II) complex. [14,16] Paramagnetic adducts with  $\text{O}_2$  are also formed. Naccache and co-workers propose formation of a  $\mu$ -peroxo binuclear rhodium(II) species, formed from the oxidation of rhodium(I) ions by  $\text{O}_2$ . [14] This complex is thought to have  $\text{C}_{3v}$  symmetry. It is also postulated that the formation of the CO- and  $\text{O}_2$ - adducts involve different rhodium sites. When the  $\text{O}_2$ - adduct is exposed to water, a new paramagnetic species is observed. Naccache and co-workers propose a double trigonal bipyramidal structure for this complex, linked through the  $\mu$ -peroxo bridge. [14] A paramagnetic species is also formed when NO is adsorbed onto the activated rhodium zeolite. Atanasova and co-workers propose a complex containing two NO molecules coordinated to a single rhodium(II) ion. [17]



Ruthenium zeolites are prepared by ion exchange of  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  onto NaY zeolite. The high temperature activation treatment completely decomposes the ammine complex. No EPR signal is observed following the dehydration treatment. Upon adsorption of CO, two different paramagnetic species are observed, depending on the pressure of CO used. Gustafson and co-workers propose formation of a monocarbonyl complex of ruthenium(III) at low pressures.[18] When excess CO is present, di- or tri- carbonyl species are formed. Adsorption of  $\text{O}_2$  on the activated zeolite is thought to produce  $\text{RuO}_2$  in the zeolite. Adsorption of  $\text{O}_2$  on the monocarbonyl adduct produces a new paramagnetic species with the unpaired electron localized mainly on the oxygen. Gustafson and co-workers propose formation of a monocarbonyl ruthenium(IV) superoxide species.[18]

$[\text{Ru}(\text{III})(\text{bpy})_3]^{3+}$  is known to promote the photochemical dissociation of water.[19] Quayle and Lunsford have prepared a  $[\text{Ru}(\text{III})(\text{bpy})_3]^{3+}$  complex within the cages of Y zeolite.[20] The complex, too large to be ion exchanged into the zeolite, is formed in the super cage from reaction of 2,2'-bipyridine with  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  with subsequent oxidation by  $\text{Cl}_2$ . This species has been characterized by EPR spectroscopy.

EPR studies in conjunction with other physical techniques are being used to probe the sites at which substrates react with transition metals to form weakly bonded complexes which may be analogous to intermediates in many catalytic systems.

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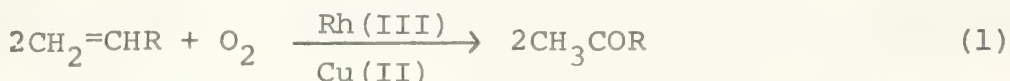
The Specific Oxidation of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  by  $\text{O}_2$   
Via the Coordination of in situ Generated  $\text{HOOH}$ .  
Implications for the  $\text{Rh}(\text{III})/\text{Cu}(\text{II})$  Catalyzed  $\text{O}_2$  Oxidation  
of 1-Alkenes to 2-Ketones

Eric D. Nyberg

Final Seminar

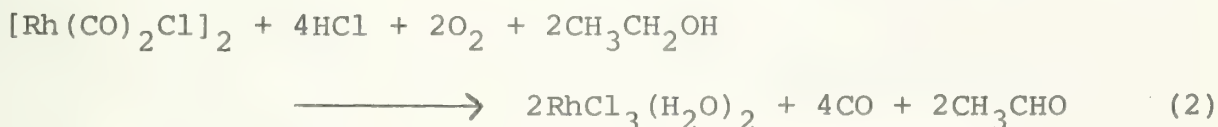
April 27, 1982

The principle aim in homogeneously catalyzed oxidations of hydrocarbons is a high degree of product specificity. Unfortunately, most oxidations involve free radical processes which are generally very unspecific. Exceptions are found for cases in which the bond breaking and reforming steps occur primarily at a well defined catalyst center. Over the past decade a new class of homogeneous catalytic oxidations involving non-free radical, non-Wacker type,  $\text{O}_2$  oxidation of terminal olefins have been reported [1-5]. These systems are in general quite specific and are indeed proposed to proceed by the coordination of both olefin and dioxygen to the catalyst where they react to form products. The most exceptional case is the  $\text{Rh}(\text{III})/\text{Cu}(\text{II})$  catalyzed  $\text{O}_2$  oxidation of 1-alkenes to 2-ketones in ethanol with  $\geq 98\%$  specificity [1] (reaction 1).



In this system it has been proposed that an initiation step involving the ethanol reduction of  $\text{Rh}(\text{III})$  to a  $\text{Rh}(\text{I})$  catalyst is occurring.

On investigating reaction 1 we made a number of observations which could not be accounted for assuming the catalyst was a rhodium(I) complex. These include a marked enhancement of reaction rates and catalyst stability at greater chloride concentrations, and the observation of induction periods preceding the 1-hexene oxidations when using  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  as the catalyst precursor in the absence of  $\text{Cu}(\text{II})$  (which are not observed using  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ). As a result we chose to investigate the oxidation of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  under conditions typical for the catalytic oxidation of 1-hexene, and found  $\text{RhCl}_3(\text{H}_2\text{O})_2$  to be formed stoichiometrically (reaction 2). As expected the  $\text{RhCl}_3(\text{H}_2\text{O})_2$  produced in reaction 2 was an active



catalyst for reaction 1, and did not exhibit the induction period found when using  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ . This, in addition to our ruling out the alcohol reduction of  $\text{Rh}(\text{III})$  to  $\text{Rh}(\text{I})$  as proposed earlier [1], indicates the active catalyst for this reaction is a rhodium(III) chloride.



On investigating reaction 2 in detail an unusual mechanism was discovered involving the in situ ethanol reduction of  $O_2$  to  $HO_2H$ , which subsequently coordinates to  $[Rh(CO)_2Cl]_2$  forming a surprisingly stable hydroperoxorhodium intermediate (I). There are few examples in the literature of hydroperoxo or alkylperoxo complexes of the platinum metals [6-10] (other than those with bio-type or Schiff base ligands). The first evidence for the role of  $HO_2H$  in reaction 2 was obtained from the rate law determined for this reaction (equation 3), which is independent of the concentration of  $[Rh(CO)_2Cl]_2$ . This rules out a mechanism involving as a first

$$\frac{d[I]}{dt} = k[H^+][O_2] \quad (3)$$

step the formation of a hydride complex resulting from the oxidative addition of  $HCl$  to  $[Rh(CO)_2Cl]_2$ , followed by a reaction with  $O_2$ , which has been proposed to occur in several other systems [10,11]. Indeed, equation 3 indicates an intermediate oxidant is being formed from the acid catalyzed reaction between ethanol and  $O_2$  in the initial step(s) of reaction 2. This was confirmed by using aqueous  $HO_2H$  to directly oxidize  $[Rh(CO)_2Cl]_2$ , producing  $RhCl_3(H_2O)_2$  via the same intermediate I. The reduction of  $O_2$  to  $HO_2H$  by 1° and 2° alcohols has been known for a long time, producing  $HO_2H$  using AIBN as an initiator [12] and  $H_2O$  in the presence of metal oxide catalysts [13] due to their efficient decomposition of  $HO_2H$ . I has been characterized as  $H_2[Rh(CO)Cl_2(OOH)]$  by FT-IR, electronic absorption spectroscopy, and its chemical characteristics. For example, I seems to be capable of both oxidizing  $CO$  to  $CO_2$  and 1-alkenes to 2-ketones, and exhibits decomposition characteristics expected for a hydroperoxide complex.

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# Activation of Dioxygen

Barry B. Corden

Final Seminar

May 13, 1982

Oxidations of organic compounds are thermodynamically favorable, yet this spin-forbidden reaction usually is kinetically sluggish. Numerous biological and industrial processes require (1) the partial oxidation of a substrate and (2) a reasonably fast reaction rate. One way to accelerate these spin-forbidden reactions may be to employ metal-dioxygen complexes ( $M-O_2$ ) as reagents or catalysts since the dioxygen spin state and basicity changes upon coordination. Hence, dioxygen binding and activation by transition metals has been studied intensively [1] to elucidate the factors that influence metal-dioxygen bond formation and the electronic structure of the resultant adduct.

The cobalt-dioxygen complexes are of particular interest because adduct formation is reversible yet they are sufficiently stable for facile characterization and study. This unusual paramagnetic complex forms when two unpaired electrons spin-pair upon  $O_2$  coordination. The remaining unpaired electron resides exclusively on the dioxygen ligand and indirectly spin-polarizes the cobalt d-orbitals[2].

The purpose of the investigation described herein is to demonstrate direct activation of dioxygen by a metal does occur, and to observe changes in the character of the dioxygen ligand as the ligand field strength about the metal is altered.

Van Dort reports that substituted phenols are converted catalytically to the corresponding quinones by cobalt complexes [3]. Results of kinetic and mechanistic studies support a reaction scheme [Figure 1] where cobalt-dioxygen is required in two distinct steps in the catalytic cycle. Mechanisms responsible for catalyst [Figure 2] deactivation are described briefly [4].

## PROPOSED MECHANISM

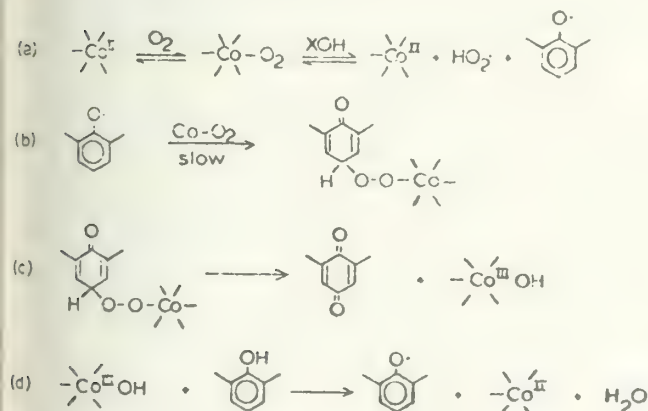


Figure 1

## Probable conformation of Co(SMDPT)

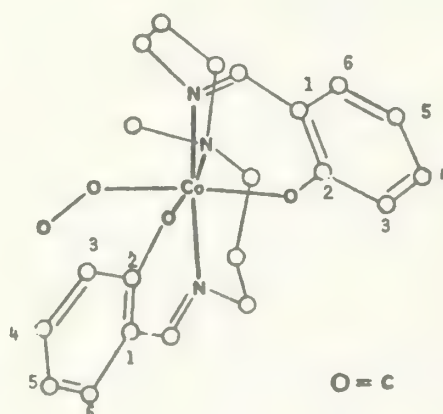


Figure 2



The role of ligand substituents on the reaction rate and product distribution are dramatic. Preliminary studies show that catalyst modification can (a) lead to steric blocking of the active site or (b) alter the basicity of the dioxygen ligand. Finally, the catalyst attacks carbon-carbon double bonds. Several reactions of this type are discussed [for example, Figure 3] [5]. Evidence is presented to support the direct attack of a metal activated dioxygen on the double bond.

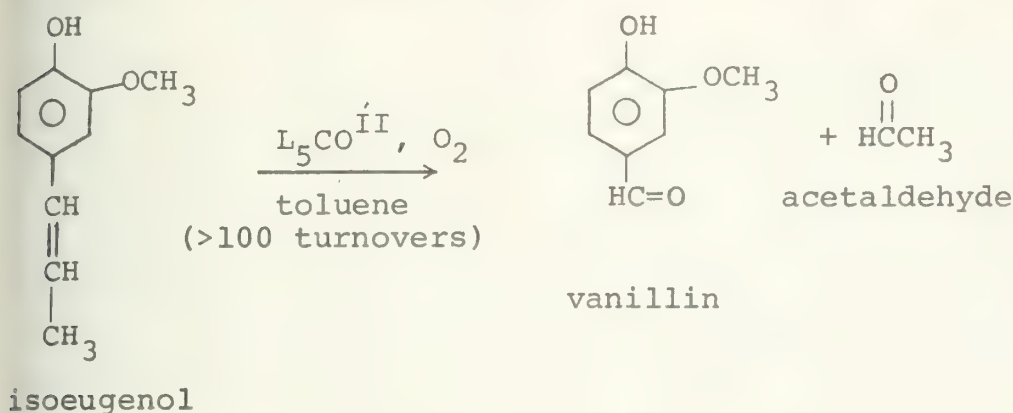


Figure 3

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Structure in figure 2 is based on  $\mu$ -oxo dimer, see Lindblom, Schaefer, and Marsh, Acta. Crystallogr., B, 1971, 27, 1461.

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# Applications of Flash Vacuum Pyrolysis and Related Studies on Alkyne Trimetallic Clusters

Allen D. Clauss

Final Seminar

May 18, 1982

The study of organometal cluster compounds in recent years has provided a wealth of new information concerning the possible bonding modes and reaction pathways for hydrocarbons interacting with multi-metal centers. Coordinatively unsaturated clusters and "lightly stabilized" derivatives have played an important role in the development of this chemistry.[1] Unlike the majority of coordinatively saturated clusters, these compounds are highly reactive at room temperature and below facilitating the characterization of thermally unstable intermediates. Unfortunately, very few highly reactive metal cluster compounds of this sort have been synthesized and the further development of mechanistic organometal cluster chemistry is limited by the small number available.

As a new approach to this problem we have employed the technique of flash vacuum pyrolysis (FVP) to generate reactive organometallic clusters and to induce novel structural rearrangements. This technique, which has been used by organic chemists for more than 15 years, is characterized by high vacuum distillation of the reactant through a heated tube where contact times are short ( $10^{-3}$  to  $10^{-1}$  sec) followed by rapid condensation of the products at low temperature.[2]

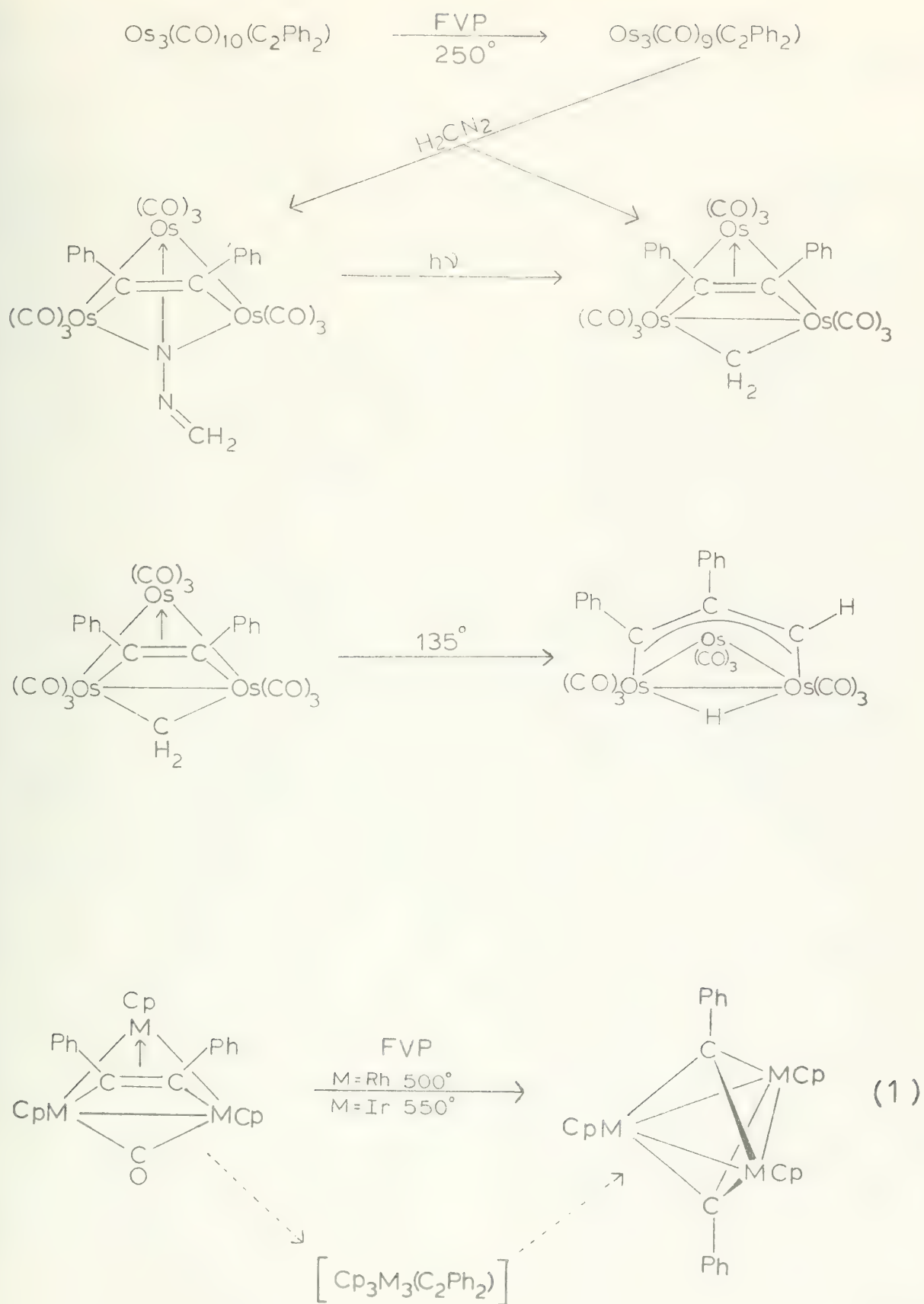
Flash vacuum pyrolysis of  $\text{Os}_3(\text{CO})_{10}(\text{C}_2\text{Ph}_2)$  at  $250^\circ\text{C}$  results in efficient decarbonylation to yield coordinatively unsaturated  $\text{Os}_3(\text{CO})_9(\text{C}_2\text{Ph}_2)$ . [3] The ability to cleanly generate this highly reactive compound has allowed its isolation and complete characterization as well as a systematic investigation of its reactivity. One of the most remarkable reactions is that of  $\text{Os}_3(\text{CO})_9(\text{C}_2\text{Ph}_2)$  with diazomethane. [4] This reaction proceeds rapidly at room temperature to yield nearly equal amounts of a thermally stable  $\mu$ -diazomethane adduct and a  $\mu$ -methylene complex. Photolysis of the diazomethane complex converts it into the methylene derivative by intramolecular loss of dinitrogen. Furthermore, heating a solution of the methylene complex results in coupling of the methylene and diphenylacetylene ligands to yield a new cluster containing a face bonded dimetallallyl ligand. (Scheme)

Related studies have been carried out on the compounds  $\text{Cp}_3\text{M}_3(\text{CO})-\text{C}_2\text{Ph}_2$  ( $\text{M} = \text{Rh}, \text{Ir}$ ). [5] Although these are isoelectronic with  $\text{Os}_3(\text{CO})_{10}(\text{C}_2\text{Ph}_2)$  they exhibit a pronounced difference in behavior when subjected to FVP. The rhodium and iridium compounds were unreactive at the temperature used to decarbonylate  $\text{Os}_3(\text{CO})_{10}(\text{C}_2\text{Ph}_2)$  ( $250^\circ\text{C}$ ). At higher temperatures ( $500$ - $600^\circ\text{C}$ ) decarbonylation occurs; however, it is accompanied by alkyne cleavage to yield stable bisalkylidyne clusters. [6] (equation 1) Additional experiments established that the alkyne cleavage occurs intramolecularly on the trimetallic framework. Although alkyne cleavage has previously been shown to occur at metal surfaces to yield surface carbyne fragments, [7] it has not been established how many metal centers are required to facilitate cleavage of the carbon-carbon triple bond. This organometallic model system establishes the viability of a trimetal center as a template for the decoupling of an alkyne.





# Scheme:





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Saturated Hydrocarbon Chains as Propagators of  
Magnetic Exchange Interaction Between Ti(III) Metallocenes

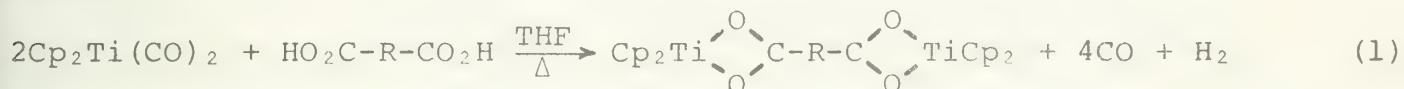
Arrietta W. Clauss

Final Seminar

June 22, 1982

The study of extended organic ligands as mediators of electron transfer between two metal ions is of continuing interest.[1] In several biological electron-transport chains it is generally believed that electrons are transferred between metal ions that are separated by distances greater than 20 Å.[2] It is possible that the electrons transfer via saturated residues in the polypeptide chains. The study of magnetic exchange interactions in binuclear complexes indirectly characterizes the viability of a given organic ligand to mediate electron transfer between the two metal centers.

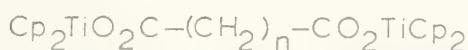
The present study was undertaken to ascertain whether a magnetic exchange interaction between two metal ions could be propagated by saturated hydrocarbon chains and to determine the number of carbon atoms through which an exchange interaction could be detected. Titanium(III) metallocenes bridged by the dianion of a dicarboxylic acid proved to be a convenient system to examine. The dicarboxylic acids provide an organic ligand which can be systematically varied. The presence of only one unpaired electron per  $Ti^{3+}$  ion facilitates the interpretation of the physical data. The air sensitive dimers are synthesized according to equation (1), [3,4] where R is a hydrocarbon:



The compounds have been characterized by mass spectral, microanalytical and infrared data.

Variable temperature (4.2-300 K) magnetic susceptibility was used to characterize the exchange interaction in the solid state (see Table 1).

Table 1



| <u>n</u> | <u>-J (cm<sup>-1</sup>)</u> |
|----------|-----------------------------|
| 1        | 2.6                         |
| 2        | 1.6                         |
| 3        | 0.8                         |
| 4        | —                           |
| 6        | —                           |
| 8        | —                           |
| 10       | —                           |

Weak antiferromagnetic exchange interactions are observed in the Ti dimers bridged by the dianions of malonic (n=1), succinic (n=2) and





glutaric (n=3) acids. There is a monotonic decrease in the magnitude of the antiferromagnetic exchange interaction as the number of methylene carbon atoms in the chain is increased. No interaction is observed in the binuclear Ti complexes with longer chains, n=4,6,8,10.

The monotonic decrease in the exchange parameter in the solid state suggests that the interaction is intramolecular and propagated by the carbon atoms of the bridging unit. Binuclear  $Ti^{3+}$  complexes bridged by the dianions of alkyl-substituted and cyclic dicarboxylic acids were investigated to clarify the pathway of the exchange interaction. The additional bulk of the substituents decreases the intermolecular contacts and the rigid framework of the cyclic systems ensures that the intramolecular magnetic exchange interactions are not occurring directly by contact of the  $(\eta^5-C_5H_5)_2Ti$  units via a folded conformation. The presence of antiferromagnetic exchange in these complexes supports the intramolecular nature of the interaction.

Electron paramagnetic resonance (EPR) was used to characterize the exchange interaction in solution. The titanium hyperfine splitting pattern observed in the room temperature X-band EPR spectra indicates that the exchange interaction is greater than  $10^{-3} cm^{-1}$ . [5] Variable temperature (3-12 K) EPR studies were conducted to assess the magnitude of the exchange interaction. [6] The results are complicated by microwave power saturation of the EPR signal. Evidence for intramolecular exchange interactions is obtained for the  $Ti^{3+}$  complexes bridged by malonate (n=1), glutarate (n=3) and adipate (n=4).

Several monomeric complexes of the general formula  $Cp_2TiO_2CX$  (X=hydrocarbon) have also been studied to determine whether an intermolecular exchange can be detected in the solid state. With one exception the monomers showed no detectable exchange interaction. The benzoate derivative  $Cp_2TiO_2CC_6H_5$  exhibited a significant intermolecular exchange in the solid state. Single crystal X-ray diffraction studies on two Ti dimers and the benzoate monomer have helped to identify the possible pathways for the exchange interaction.

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# Structural, Catalytic, and Intercalation Chemistry of Clay Minerals

Warren L. Nehmer

Final Seminar

July 13, 1982

Chemical processes involving clay minerals are of vital importance in such fields as petroleum engineering, refining, waste disposal, and the paper industry.[1] Despite the importance of clay minerals, only recently with the advent of new and improved spectroscopic techniques, has the complex chemistry of clay minerals begun to be understood. The present study was undertaken in an effort to understand more fully three aspects of clay chemistry. These three areas are: 1) the oxidation-reduction reactions of structural iron in high iron containing clays; 2) the use of clay minerals as supports for catalytic reactions; and 3) the effect of intercalation on the electronic structure of transition metal complexes.

Ballet and coworkers[2] have determined that the 1:1 clay mineral greenalite is highly two dimensional in regards to its magnetic properties. They determined that the iron atoms within the plane of the clay crystallite order ferromagnetically at 24K, and then adjacent sheets order antiferromagnetically at lower temperatures. The magnetic properties of a series of lepidomelanes with structural  $\text{Fe}^{2+}$  ranging from 95 to 7 percent of the total iron, indicate that the ferromagnetic character of this clay is directly related to the  $\text{Fe}^{2+}$  content. The value of  $(\text{XT})_{\text{max}}$  varies linearly with percent  $\text{Fe}^{2+}$  suggesting that the oxidation of  $\text{Fe}^{2+}$  ions in the clay layers proceeds from the edges of the crystallites inward, as contrasted with an oxidation that occurs randomly throughout each layer.

The use of clay minerals as supports for transition metal catalysts has been receiving much attention in the last decade.[3] Cation exchanged Cu(II)-clays with various amine ligands were found to catalyze the oxidative coupling of 2,6-dimethylphenol, leading to the quinone dimer or the polyphenylene oxide polymer, depending on the reaction conditions. The reaction rate is dependent on the phenol's ability to diffuse into the interlamellar region of the clay as determined by X-ray diffraction and  $\text{O}_2$  uptake experiments

Ferrocene can be intercalated and oxidized via electron transfer by the layered material  $\text{FeOCl}$ .[4] Clay minerals with exchangeable cations have been found to oxidize and intercalate a variety and ferrocene monomers and dimers. Dimers such as biferrocene and bis(fulvalene)diiron are intercalated into the clay as the mixed valent monocations. The clay environment seems to have no effect on the electron transfer rate of biferrocene and bis(fulvalene)diiron as judged by  $^{57}\text{Fe}$  Mössbauer spectroscopy. The biferricenium-clay sample has an outer quadrupole-split doublet of 2.15 mm/sec and an inner doublet of 0.49 mm/sec. This compares to 2.12 mm/sec and 0.38 mm/sec for biferricenium  $^+\text{I}_3^-$ . [5] The bis(fulvalene)diiron clay sample has a quadrupole splitting of 1.77 mm/sec as compared to 1.76 mm/sec for bis(fulvalene)diiron  $^+\text{I}_5^-$ . From X-ray diffraction data and orientation studies using EPR, it is suggested that the bis(fulvalene)diiron molecule is intercalated into the clay so that the fulvalene planes lie perpendicular to the clay layers.





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The Chemistry of  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$ 

David A. Lesch

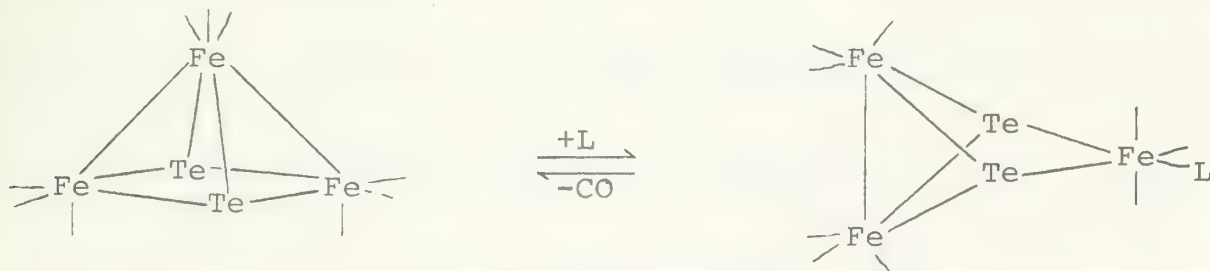
Final Seminar

July 20, 1982

The tellurium analogs of the two well-studied classes of transition-metal nonmetal clusters  $\text{Co}_3(\mu_3\text{-E})(\text{CO})_{9,12}$  ( $\text{E} = \text{CR}, \text{SiR}, \text{GeR}, \text{SnR}, \text{P}, \text{As}, \text{Sb}, \text{S}, \text{Se}$ ) [1] and  $[\text{M}(\mu\text{-E})(\text{CO})_3]_{2,4}$  ( $\text{M} = \text{Co}, \text{Fe}$ ;  $\text{E} = \text{P}, \text{As}, \text{Sb}, \text{S}, \text{Se}$ ) [2] have not been reported. This fact plus the observation that when the covalent radius of E [ $r_{\text{COV}}(\text{E})$ ]  $\leq 1.22\text{\AA}$  the cluster is totally M-M bonded and when  $r_{\text{COV}}(\text{E}) \leq 1.40\text{\AA}$  the cluster is totally M-M nonbonded suggests that there might be unique properties associated with first row transition-metal clusters containing tellurium ( $r_{\text{COV}} = 1.36\text{\AA}$ ). Evidence for unusual reactivity has long been recognized for  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$ , which, unlike  $\text{Fe}_3(\mu_3\text{-S})_2(\text{CO})_9$  or  $\text{Fe}_3(\mu_3\text{-Se})_2(\text{CO})_9$ , forms stable Lewis base adducts [3]. Previous workers suggested that this difference in reactivity was due to coordination of the Lewis base to tellurium [4].



The structure of the Lewis base adducts of  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$  was deduced by  $^{125}\text{Te}$  NMR spectroscopy while  $^{31}\text{P}$  NMR studies on the binding of bidentate ligands established the extreme facility of adduct formation [5]. The crystal structure of  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9\text{PPh}_3$  confirmed our NMR results and demonstrated that the conversion of  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$  to its  $\text{PPh}_3$  adduct involved the scission of one Fe-Fe bond thus representing a nido to arachno conversion:



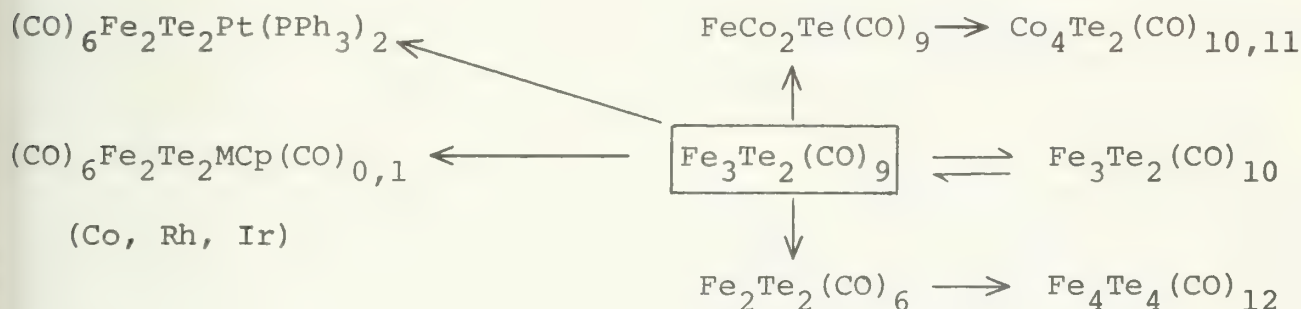
Thermal or chemical ( $\text{Me}_3\text{NO}$ ) decarbonylation of the characteristically orange adducts gives substituted products which are spectroscopically similar to the purple  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$ . The maximum extent of substitution



is dominated by steric effects: ligands of large cone angle give disubstitution, those of intermediate cone angle give tri- or tetrasubstitution and lastly, very compact ligands (eg.  $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ ) yield the hexasubstituted cluster.

$\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$  can be obtained in ~90% yield from the thermal decarbonylation of  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_{10}$  which in turn is prepared via the reduction of  $\text{TeO}_3^{2-}$  by  $\text{HFe}(\text{CO})_4^-$ . A minor product (<10%) in this synthesis is  $\text{Fe}_2(\mu\text{-Te}_2)(\text{CO})_6$  [6]. Although it is a useful precursor to mixed-metal clusters,  $\text{Fe}_2(\mu\text{-Te}_2)(\text{CO})_6$  is relatively unstable with respect to its dimer,  $\text{Fe}_4(\mu_3\text{-Te})_4(\text{CO})_{12}$ , which in analogy to  $\text{Co}_4(\mu_3\text{-Sb})_4(\text{CO})_{12}$  has the cubane structure.  $\text{Fe}_2(\mu\text{-Te}_2)(\text{CO})_6$  can also be generated in situ from  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$  in MeCN and this process forms the basis for the reactions described below.

$\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$  reacts with  $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$  to give  $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Te})_2\text{-Pt}(\text{PPh}_3)_2$  whose structure, based on analogy with the crystallographically defined  $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Se})_2\text{Pt}(\text{PPh}_3)_2$ , is similar to  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9(\text{PPh}_3)$  [7]. Its  $^{125}\text{Te}$  NMR chemical shift of -861 ppm is also similar to the adduct ( $\delta$ -887 and -938 ppm). The chemical shifts of these arachno clusters are in sharp contrast to those of the nido  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_{9-n}\text{Ln}$  ( $\delta$ ~+1100 ppm). This same chemical shift pattern was observed for the isoelectronic compounds  $(\text{CO})_6\text{Fe}_2(\mu_3\text{-Te})_2\text{MCp}(\text{CO})_{0,1}$  ( $\text{M} = \text{Co}, \text{Rh}$ ) which were prepared from  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$  and  $\text{CpM}(\text{CO})_2$ . Reaction of excess  $\text{Co}_2(\text{CO})_8$  with  $\text{Fe}_3(\mu_3\text{-Te})_2(\text{CO})_9$  results in sequential replacement of iron to ultimately give  $\text{Co}_4(\mu_4\text{-Te})_2(\text{CO})_{10,11}$ .



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15

# Electroinitiated Polymerization of Vinyl Monomers for the Preparation of Crosslinked Polymer Film Electrodes

Brenda R. Shaw

Final Seminar

August 6, 1982

Electrochemical devices are used for solar cells, fuel cells, batteries, electrolytic cells and electronic display devices. In all of these devices the electrode reaction depends strongly on the nature of the electrode surface. Modification of electrodes allows increased control over electrochemical processes. Two recent reviews summarize work in the chemical modification of electrodes [1,2].

In 1978, Van De Mark and Miller reported the use of an adsorbed polymer as an electrode modification layer [3]. Since that first report, numerous electrochemists have prepared and studied electrodes coated with electroactive polymers [4,5,6,7].

One of the major reasons for interest in polymer-modified electrodes is the prospect for their use in surface electrocatalysis [8]. Criteria for useful catalyst supports in heterogeneous electrocatalysis are similar to criteria for heterogeneous thermal catalysis on polymer resin supports [9]. An ideal electrocatalytic system for use in synthesis would contain a thick, porous film of catalyst-containing material attached to an electrode surface. The catalyst throughout the film should be easily accessible to substrate species. In addition, charge transport and ion mobility within the film should be facile. One system which has promise in meeting these criteria is an electroactive, crosslinked polymer film adsorbed to an electrode in a swelling solvent.

There have been several reports of methods for obtaining crosslinked polymer films on electrodes. These include radiofrequency plasma polymerization [10], ultraviolet [11] and gamma [12] irradiation of polymer films, electrochemically induced dimer formation between polymer pendant groups [13], and electroinitiated polymerization of multifunctional electroactive monomers [14]. These methods produce useful films but are dependent upon the specific properties of the crosslinking agent used, or yield films of unknown structure.

The goal of the work reported in this seminar was to develop an electrochemical method that would be general for preparing polymer films and that would give films of known structure. Polyvinylbenzophenone has been used as an initiator precursor for bulk graft copolymerization. The poly-anion radical initiator was generated electrochemically for the polymerization of methylmethacrylate [15], and the polydianion initiator was generated by chemical reduction for the polymerization of styrene [16].

Based on the success with polyvinylbenzophenone in bulk anion polymerization, benzophenone was selected for use in the present study. Polydivinylbenzene-coated platinum electrodes were prepared from divinylbenzene by generating the benzophenone dianion electrochemically in N,N-dimethylformamide with tetrabutylammonium perchlorate



as electrolyte. The polymer was sulfonated by exposing it to a solution of chlorosulfonic acid in dichloromethane, then to a solution of water in acetonitrile [17]. The resulting crosslinked polystyrene-sulfonate film was studied by carrying out cyclic voltammetry in a solution of  $\text{Ru}(\text{NH}_3)_6^{2+}$ . The ruthenium complex was ion-exchanged into the film as shown by reversible one-electron oxidation for the ruthenium complex in the film. This wave remained when the electrode was placed in supporting electrolyte solution in the absence of dissolved  $\text{Ru}(\text{NH}_3)_6^{2+}$ .

Polyvinylferrocene was produced from vinylferrocene on pyrolytic graphite in the same way in acetonitrile. In the case of vinylferrocene, however, polymerization occurred to some extent even in the absence of benzophenone.

Many metal-phosphine complexes are known to be good catalysts for reactions that may be considered formally as oxidation-reduction reactions, such as the hydrogenation of olefins [18]. Possible electrocatalytic behavior of such complexes may be investigated by attaching them to a phosphine-containing polymer on an electrode surface. With this in mind, the monomer *p*-styryldiphenyl phosphine was synthesized [19] and polymerized [20] by a radical mechanism. Metal complexes of this polymer were prepared but electrochemical studies were thwarted by irreversible electron transfer and instability of the non-crosslinking films in swelling solvents. Work is continuing on these systems.

A possible general method has been developed for the preparation of crosslinked, polymer film electrodes. Sulfonated polydivinylbenzene was prepared as an ion-exchange resin film and is stable even in water, a swelling solvent for this polymer. Application of this method to the preparation of supports containing known electrocatalysts, such as polyvinylferrocene [10], and potential electrocatalysts such as metal-phosphine complexes holds promise for future work.

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## Thermodynamic and Spectroscopic Studies of Some Metal Dimers

Rich Cosmano

Final Seminar

August 17, 1982

There has been a great deal of interest over the years concerning the structure and reactivity of multi-metal systems.[1] Some of the most intensely studied of these have been the carboxylate bridged metal dimers having the classical copper acetate structure in which four acetates bridge two metal atoms. These dimers have been investigated theoretically, structurally, thermodynamically, and spectroscopically by a host of researchers. While much has been learned about the metal carboxylates, there are still some important questions regarding the nature of adduct formation between these dimers and axial bases.

Earlier published work from this laboratory has dealt with the Lewis acid-base reactivity of rhodium trifluoroacetate,[2] rhodium butyrate,[3] rhodium heptafluorobutyrate,[4] and molybdenum heptafluorobutyrate.[4] Several conclusions have been drawn from the thermodynamic and spectroscopic results concerning the contributions which the metal core, the bridging ligands, and the axial bases make to adduct formation. Using an "E and C" type interpretation of the Lewis acid-base reactions, it has been shown that the relative electrostatic and covalent contributions to the interaction are dependent upon the electron withdrawing properties of the bridging ligands and the formal bond order of the metal-metal core. In certain instances, the results are consistent with a back donation of  $\pi^*$ -electron density from the metal to the axial ligand. The extent of this  $\pi$ -stabilization to the adduct bond again depends on the metal core and on the bridging ligands, as well as the ability of the axial base to act as a  $\pi$ -acceptor.

More recently, thermodynamic studies of ruthenium butyrate have given further support for the interpretation of the reactivity of the metal dimers in terms of the E and C correlation. The ruthenium dimer appears to undergo  $\pi$ -bonding interactions with certain bases, as was the case for the rhodium dimers. The difference between the formal positive charge of the ruthenium core (+5) and that of the rhodium or molybdenum cores (+4) is reflected in the electrostatic contributions to the enthalpies of adduct formation for each. The relative importance of the covalent and electrostatic contributions is again seen to depend upon the formal bond order.

EPR studies of the adducts of  $\text{Rh}_2(\text{OCR})_4$  and phosphine or phosphite bases by Kawamura, *et al.*, [5] led to some interesting results and conclusions concerning the interaction between the metal atoms and the axial ligands. Most importantly, they concluded that the axial bond between the metal and base was " $\sigma$ -only" in nature and that there was no need to invoke  $\pi$ -stabilization in interpreting their epr spectra, in contrast to the conclusions drawn from Drago and coworkers from their work on metal carboxylates. An extension of the epr investigation of rhodium butyrate to include other bases and conditions



has subsequently shown that the epr spectra obtained appear to be a function of the strength of the acid-base interaction rather than the type of bonding involved.

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Electron Paramagnetic Resonance Studies  
on Some Group VIII Transition Metal Complexes

James R. Stahlbush

Final Seminar

August 17, 1982

Electron paramagnetic resonance (EPR) is a technique which has come into common usage to obtain structural and electronic information about transition metal complexes.[1] This technique has been utilized to obtain structural information about a series of five coordinate cobalt(II) trisphosphine complexes and their dioxygen adducts,[2] and to determine the nature of bonding of various bases to a rhodium dimer-nitroxide spin label complex.

A series of five coordinate cobalt(II) trisphosphine complexes ( $\text{Co}(\text{PR}_3)_3\text{L}_2$ , where  $\text{R}_3 = \text{Me}_3, \text{Me}_2\text{Ph}, \text{MePh}_2$  and  $\text{L} = \text{Br}, \text{CN}$ ) and their dioxygen adducts were investigated using EPR to enhance the understanding of oxygen binding to cobalt(II) complexes and to explain the formation of an unusual cobalt dimer discovered by Halpern and co-workers[3] which possesses dioxygen bound to cobalt in a ring-bonding mode, I.



I

The  $\text{Co}(\text{PR}_3)_3\text{Br}_2$  complexes with  $g_{\parallel} \sim 2.4$  and  $g_{\perp} \sim 2.08$  and broad unresolved hyperfine of the  $g_{\parallel}$  signal are assigned a trigonal bipyramidal geometry with two phosphine ligands in axial positions and one phosphine and two bromide ligands in equatorial positions. This assignment is supported by an x-ray crystal structure of  $\text{Co}(\text{PF}_2\text{Ph})_3\text{Br}_2$ . [4] The  $\text{Co}(\text{PR}_3)_3(\text{CN})_2$  complexes with  $g_1 \sim 2.18$ ,  $g_2 \sim 2.14$  and  $g_z \sim 2.01$  and extensive hyperfine splitting in all regions due to cobalt ( $I = 7/2$ ) and phosphorus ( $I = 1/2$ ) are assigned a square pyramidal geometry with one axial phosphine and two cyanides and two phosphines in trans positions in the basal plane.

The dibromide complexes do not react with oxygen. Oxygen does react with the dicyano complexes by replacing the axial phosphine to form a five coordinate cobalt(II) dioxygen complex. This was the first time a five coordinate cobalt(II) dioxygen complex in which there are no chelating ligands was reported.[2] This unusual complex also appears to be the intermediate which leads to the formation of Halpern's[3] cobalt dimer with the ring-bonded oxygen.

There is an ongoing controversy in the literature about the ability of dirhodium tetracarboxylate dimers to undergo  $\pi$  as well as  $\sigma$  interaction with bases binding to the two axial sites.[5-10] In an effort to clarify this controversy the Q-band EPR spectra of the nitroxide spin label 2,2,6,6-tetramethylpiperidiny-1-oxy (TMPNO) bound to one rhodium of dirhodium tetra-perfluorobutyrate ( $\text{Rh}_2(\text{pfb})_4$ ) with the addition of  $\sigma$  and  $\pi$  bonding bases to the second rhodium was investigated.





Upon addition of TMPNO to  $\text{Rh}_2(\text{pfb})_4$  the  $g$  value of TMPNO increases 0.0105 from 2.0047 to 2.0152. This same effect was first observed with  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  [11] and is the largest  $g$  shift ( $\Delta g$ ) yet reported for a bound nitroxide. Binding various bases (B) to the second rhodium atom causes a decrease in  $\Delta g$  of the bound TMPNO indicating a decreased Rh-TMPNO bond strength. The values of  $\Delta g$  range from 0.0083 for ethyl acetate, a weak base, to 0.0025 for piperidine, a strong base. Thus as the B-Rh bond strengthens the Rh-TMPNO bond weakens. To quantify this effect the E and C equation was utilized. [12]

$$-\Delta H = E_A E_B + C_A C_B$$

The  $E_A$  and  $C_A$  numbers for  $\text{Rh}_2(\text{pfb})_4$  had previously been determined [9] as well as the  $E_B$  and  $C_B$  numbers for the bases studied. [12] Thus the heats of formation,  $-\Delta H$ , due to the  $\sigma$  only interactions between  $\text{Rh}_2(\text{pfb})_4$  and bases were determined and a linear relationship was found between  $-\Delta H$  and  $\Delta g$  for most of the bases. However, some bases, most notably acetonitrile and pyridine, were found to deviate substantially from this correlation in a manner which indicates  $\pi$  bonding must also be present. These results are in good agreement with previously published thermodynamic results. [5,6,9]

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## The Sonochemistry of Some Metal Carbonyl Complexes

Paul F. Schubert

Final Seminar

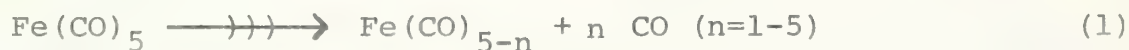
September 23, 1982

Ultrasonic irradiation of solutions gives rise to a variety of effects including emulsification, ultrasonic cleaning, sonoluminescence, and chemical reactions [1,2]. The chemical action of ultrasound was first recognized in 1927 by Richards and Loomis [3], and is not due to a direct interaction between the sound and molecules, but to a phenomenon associated with it called acoustic cavitation [4]. This is the formation, growth, and collapse of gas bubbles in solution due to the action of the positive and negative pressure waves of the sound on the bubbles. During collapse of the cavities, temperatures of about 3000 K and pressures of about 300 atmospheres are reached within the bubble [5]. The primary goals of this research have been: to establish the ability of organic solvents to support sonochemical reactions with appreciable rates; to determine whether cavitation phenomena could induce sonochemical ligand dissociation and ligand substitution; and to determine whether the high temperatures and pressures attained within the cavity upon collapse could produce catalytic reactions normally performed only at elevated temperatures and pressures.

All sonications were performed using a Heat Systems-Ultrasonics model W375 Sonicator cell disruptor, which consists of a 20 kHz high voltage generator rated at 375 watts and a lead zirconate-titanate piezoelectric transducer driving a titanium amplifying horn. The sonicator was used primarily in the immersion tip configuration with the probe inserted into the solution. The reaction temperature was controlled using a constant temperature bath.

The majority of sonochemical reactions have been in aqueous solution [1,2] and it has generally been assumed that they "do not take place in pure organic liquids" [6]. Thus it was necessary to establish that sonochemistry did occur in a wide range of organic solvents. The reaction chosen for study was the bleaching of the stable free radical diphenylpicrylhydrazyl (DPPH), which is a standard free radical trap [7]. Bleaching of DPPH was observed in all of the solvents attempted, indicating that these liquids will support sonochemical reactions. Further work in our group [8] found that the primary factor influencing the extent of cavitation, and thus the rate of DPPH bleaching, is the vapor pressure of the solvent.

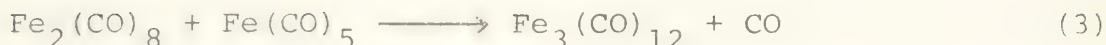
The iron carbonyls were chosen as the initial metal carbonyl for study because of their well studied thermal and photochemical reactivities [9,10,11]. Sonication of  $\text{Fe}(\text{CO})_5$ , neat or in hydrocarbon solvents, yields  $\text{Fe}_3(\text{CO})_{12}$  and finely divided pyrophoric iron. The primary process induced by sonication may be described by reaction 1.



Production of  $\text{Fe}_3(\text{CO})_{12}$  probably results from initial sonochemical production of  $\text{Fe}(\text{CO})_3$ , which may then react according to reactions 2 and 3







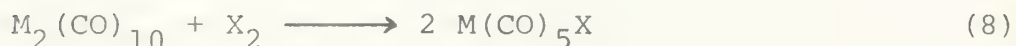
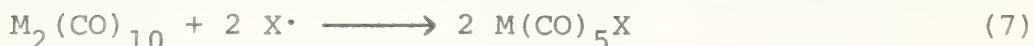
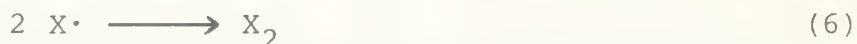
Another possible mechanism would produce  $\text{Fe}_2(\text{CO})_8$  through dimerization of  $\text{Fe}(\text{CO})_4$ . The metallic iron produced may be due to initial loss of all carbonyls or spontaneous loss of CO from clusterification of  $\text{Fe}(\text{CO})_2$  and  $\text{Fe}(\text{CO})$ .

In the presence of phosphorus donor ligands, L,  $\text{Fe}(\text{CO})_5$  undergoes thermal, photochemical, and sonochemical substitution to yield a mixture of mono- and disubstituted iron carbonyls as shown below.



The thermal and photochemical reactions both proceed through initial substitution of one CO, giving  $\text{Fe}(\text{CO})_4\text{L}$ , which then undergoes a second substitution to give  $\text{Fe}(\text{CO})_3\text{L}_2$ . In the ultrasonic substitution both  $\text{Fe}(\text{CO})_4\text{L}$  and  $\text{Fe}(\text{CO})_3\text{L}_2$  are formed simultaneously, and  $\text{Fe}(\text{CO})_4\text{L}$  does not yield  $\text{Fe}(\text{CO})_3\text{L}_2$  when sonicated in the presence of L. This again suggests the formation of  $\text{Fe}(\text{CO})_3$  in the cavitation space. The sonochemical substitution of  $\text{Cr}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ , and  $\text{W}(\text{CO})_6$  proceed in a similar manner, producing  $\text{M}(\text{CO})_4\text{L}_2$  and  $\text{M}(\text{CO})_5\text{L}$  simultaneously. Sonication of  $\text{M}(\text{CO})_5\text{L}$  in the presence of phosphines again does not produce any disubstituted products.

The considerable recent interest [12,13,14,15] in the substitution reactions of the Group VIIB metal carbonyls led us to investigate their sonochemical reactions. Sonication of  $\text{M}_2(\text{CO})_{10}$  ( $\text{M}=\text{Mn}, \text{Re}$ ) in  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CHBr}_3$ , and  $\text{CHBr}_2\text{CHBr}_2$  yields  $\text{M}(\text{CO})_5\text{X}$  in high yield. Unlike the photochemical reaction [16], sonication of  $\text{M}_2(\text{CO})_{10}$  in benzyl chloride does not yield  $\text{M}(\text{CO})_5\text{Cl}$ . This suggests that the sonochemical route to  $\text{M}(\text{CO})_5\text{X}$  does not involve initial metal-metal bond cleavage. Furthermore, the rate of reaction is independent of the metal carbonyl concentration. We propose the following mechanism for  $\text{M}(\text{CO})_5\text{X}$  production.



Sonication of  $\text{Mn}_2(\text{CO})_{10}$  in the presence of phosphines and phosphites produces  $\text{Mn}_2(\text{CO})_8\text{L}_2$ . Both  $\text{Re}_2(\text{CO})_{10}$  and  $\text{MnRe}(\text{CO})_{10}$  fail to react sonochemically with these ligands. In addition, sonication of  $\text{Mn}_2(\text{CO})_{10}$  with  $\text{Re}_2(\text{CO})_{10}$  does not yield  $\text{MnRe}(\text{CO})_{10}$  nor does the reverse reaction



occur sonochemically. Probable explanations for the behavior of  $\text{Re}_2(\text{CO})_{10}$  and  $\text{MnRe}(\text{CO})_{10}$  are that cavitation heating is insufficient to break the stronger metal-metal bond in these species, or that their volatility is too low for them to be in significant concentration within the cavitation space, and thus they cannot undergo substitution.

Homogeneous hydrogenation of CO is typically performed [17,18,19] at temperatures of 200-300°C and pressures of from 200-1500 atmospheres. Since cavitation produces high local temperatures and pressures, experiments to determine whether sonication of CO and  $\text{H}_2$  in the presence of  $\text{Co}_2(\text{CO})_8$ ,  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Rh}_6(\text{CO})_{16}$ , and  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  would produce any hydrocarbons upon sonication at 1 atmosphere. Sonication of CO and  $\text{H}_2$  in sulfolane, THF, and N-methylpyrrolidine all yielded  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  at average rates of 20 and 4.5  $\mu\text{M}/\text{min}$  respectively. Sonication in the presence of  $\text{Ru}_3(\text{CO})_{12}$  with or without iodide promoters, rhodium (from  $\text{Rh}_6(\text{CO})_{16}$  or  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ ) with or without sodium or cesium promoters,  $\text{Os}_3(\text{CO})_{12}$ , or  $\text{Co}_2(\text{CO})_8$  gave no additional hydrocarbon production. The IR of the  $\text{Ru}_3(\text{CO})_{12}$  solution after sonication under  $\text{H}_2$  and CO indicated formation of  $\text{Ru}(\text{CO})_5$ .  $\text{Ru}(\text{CO})_5$  was not produced at appreciable rates in the presence of CO or  $\text{H}_2$  alone. In a similar manner, sonication of  $\text{Os}_3(\text{CO})_{12}$  under  $\text{H}_2$  and CO slowly produced  $\text{Os}(\text{CO})_5$ . Under CO and hydrogen,  $\text{Co}_2(\text{CO})_8$  reacted to give the clusters  $\mu^3\text{-CH}[\text{Co}(\text{CO})_3]_3$  and  $\text{Co}_4(\text{CO})_{12}$ , plus an intractable solid. When this reaction was carried out under Ar its rate increased several fold.

This research has demonstrated that ligand dissociation and substitution of metal carbonyls may be brought about sonochemically, and that multiple simultaneous CO dissociation is likely in the case of iron and chromium carbonyls. It is possible that the ability of a metal carbonyl to undergo sonochemical reactions is influenced by its ability to enter the cavitation space. These reactions are possible in a wide range of solvents with the reaction rates being greatly influenced by the vapor pressure of the solvent. In addition the solvent may exhibit primary sonochemical reactions which can affect the metal complex in solution. Finally, reduction of CO to  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  was observed at appreciable rates at low temperature and pressure in the absence of any metal species.

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# Selective Homogeneous Catalytic Methanol Homologation

Stanley A. Roth

Final Seminar

September 24, 1982

The homologation of alcohols was first reported by Wender [1] in 1949. Using the homogeneous catalyst  $\text{HCo}(\text{CO})_4$  at  $180^\circ\text{C}$  and 200 atm of synthesis gas, alcohols are homologated with the production of water as the by-product.

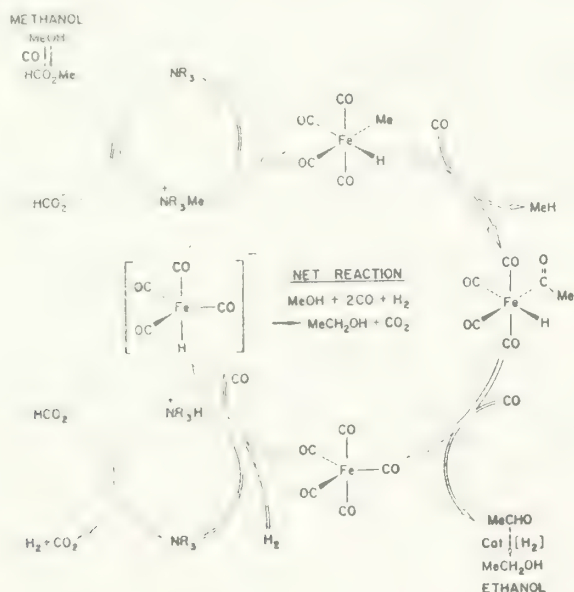


However, this reaction is intrinsically non-selective. Higher alcohols, their formate and acetate esters, glycols and acetals are produced in varying quantities depending on the reaction conditions. The reason for the lack of selectivity in the cobalt catalyzed alcohol homologation process lies in the reaction mechanism [2]. Nevertheless, there has been much effort expended to increase the selectivity of this reaction for the purpose of commercialization.

In 1979, at Argonne National Laboratory, the discovery of the catalytic homologation of methanol by  $\text{Fe}(\text{CO})_5$  in the presence of a tertiary amine has opened up a new approach to this process [3].



It is significant to note that ethanol is not homologated to propanol under reaction conditions and that  $\text{CO}_2$  (as opposed to  $\text{H}_2\text{O}$ ) is the oxygenated by-product. Methane production amounts to 20-60 mole percent of the converted methanol, depending on the reaction conditions.



The stoichiometric methyl transfer reaction from a methyl quaternary ammonium cation to metal carbonyl anions was investigated as a



model for the rate-determining step in the homogeneous catalytic homologation of methanol[4]. The second-order nucleophilic substitution reaction was demonstrated to be first-order in both  $[\text{MeNR}_3^+]$  and  $[\text{HFe}(\text{CO})_4^-]$  and zero-order in  $\text{P}_{\text{CO}}$  and  $\text{P}_{\text{H}_2}$ . In the temperature range of 180 - 210°C using N-methyl pyrrolidinone as a solvent, thermodynamic activation parameters were determined [ $\Delta\text{H}^\ddagger = 44.1$  kcal/mol,  $\Delta\text{S}^\ddagger = +16.6$  eu]. The rate of the methyl transfer reaction was observed to increase with decreasing dielectric constant and with decreasing salt concentration.

In the reaction of  $\text{MeNR}_3^+$  with  $\text{Mn}(\text{CO})_5^-$  the product selectivity to ethanol and methane was independent of  $\text{P}_{\text{CO}}$  and  $\text{P}_{\text{H}_2}$ , but was dependent on the  $\text{Mn}(\text{CO})_5^-$  concentration. At 200°C and 3600 psig of 3:1  $\text{CO}/\text{H}_2$ , the difference in second-order rate constants ( $1.99 \times 10^{-4} \text{M}^{-1}\text{s}^{-1}$  for  $\text{HFe}(\text{CO})_4^-$  and  $5.31 \times 10^{-4} \text{M}^{-1}\text{s}^{-1}$  for  $\text{Mn}(\text{CO})_5^-$ ) is an indication of the relative nucleophilicity of the metal carbonyl anions. The difference in product selectivity between the two metal systems is attributed to the presence of an intra-molecular reductive elimination mechanism competing with CO insertion for  $\text{RHFe}(\text{CO})_4$ , while for  $\text{RMn}(\text{CO})_5$ , an intermolecular reduction mechanism competing less effectively with CO insertion is required, and the resulting ethanol selectivity is correspondingly increased.

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# Molecular A-Frames: Synthesis, Structure, and Reactivity

Len Bogan

Literature Seminar

October 12, 1982

## Introduction

The first molecular A-frame complex was prepared in 1973 by the reaction of  $\text{Pd}(\text{CO})\text{Cl}$  with bis-diphenylarsinomethane(dpam) [1], but it was not correctly identified as  $\text{Pd}_2(\text{dpam})_2(\mu\text{-CO})\text{Cl}_2$  until 1977 [2]. That same year the preparation of several other A-frame complexes was reported [3]. Since then, a wealth of A-frame chemistry has been developed.

## Structure

The class of molecular A-frames is comprised of molecules sharing certain structural features. The typical A-frame geometry is shown in Figure 1. The bridging ligands which form the eight-membered ring are usually bis-diphenylphosphinomethane(dppm) or

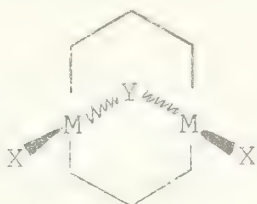


Figure 1

dpam. The terminal ligands X are halides, pseudohalides, or carbonyls. The bridging ligand Y is an atom, a small molecule, or a fragment of a molecule, capable of bridging through one or two adjacent atoms. The metal ions are low-valent Pd, Pt, Rh, or Ir, with or without a metal-metal bond. Some hetero-bimetallic A-frames have been prepared [4]. In addition to the simple case shown in Figure 1, A-frames which have additional bridging and/or terminal ligands are known.

## Synthesis and Reactivity

A-frames can be prepared by three general methods: the insertion of small molecules into the metal-metal bond of  $\text{M}_2(\text{dppm})_2\text{X}_2$  [5] ( $\text{M} = \text{Pd}, \text{Pt}, \text{Rh}$ ); the addition of a ligand to  $\text{M}_2(\text{dppm})_2\text{L}_4$  [6] ( $\text{M} = \text{Rh}, \text{Ir}$ ); and the two-center, three-fragment oxidative addition of ortho- or geminal-dihalides to  $\text{Pd}_2(\text{dppm})_3$  [7].

Reactions of molecular A-frames may be classified as one of the following types: metathesis of ligands, reactions at ligands, addition or elimination of ligands, or exchange of bridging with terminal ligands. Many observed reactions are a combination of two or more





of these types. This is true in particular of reactions catalyzed by A-frames. Two Rh A-frames are known to hydrogenate acetylenes, hydroformylate ethylene, or catalyze the water-gas shift reaction under mild conditions [8]. A Pd A-frame formed in the catalytic cyclotrimerization of dimethoxy acetylene dicarboxylate (DMAD) catalyzes this reaction [9]. A Pt A-frame catalyzes the water gas-shift reaction at very low CO pressures with some of the highest turnover rates observed for this reaction [10]. This chemistry has recently been reviewed [11].

The interesting structure and reactivity of these compounds has prompted a look at their electronic structure with extended Hückel calculations [12].

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## Intercalation of Graphite

Teng-Yuan Dong

Literature Seminar

November 11, 1982

### Introduction

The first intercalated compound, graphite sulfate, was described by Schauffaütl in 1841 [1]. However, it was only in the past decade that the value of these compounds has been discovered-namely, their application to superconductors, catalysts, and materials for batteries.

### Structure

Intercalation of graphite involves the penetration of guest species between the carbon layers with a consequent expansion of the graphite in the c-axis direction [2]. A three dimensional representation of  $C_8K$  is given in Figure 1 [3].

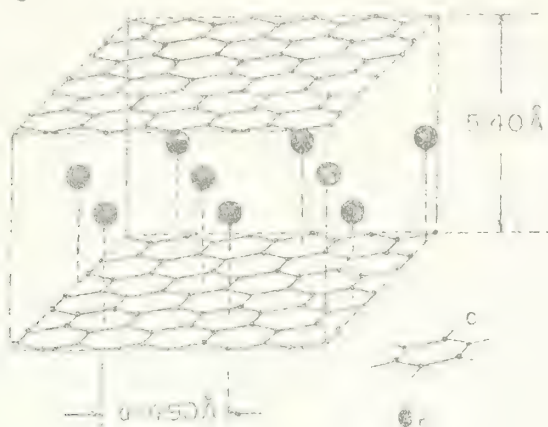


Figure 1

### Synthesis

Various metal chloride-graphites can be prepared by the use of solvent techniques [4,5]. Metal-graphites can be prepared by the diffusion of the vapors of metals at reduced pressure or by the reduction of metal chloride-graphites with  $LiAlH_4$ , or  $NaBH_4$  [6].

### Catalysis

Potassium-graphite shows distinctive reducing properties and stereochemistry towards carbonyls [7].

Chromic anhydride-graphite offers a new selective method for preparation of aldehydes from the corresponding primary alcohol [7]. An excellent review of the catalytic properties of alkali metal-graphite intercalation compounds has appeared recently and summarizes the state of the literature on this subject [8].



## Kinetic Study

It has been recognized that NMR relaxation measurements are a powerful tool for the study of molecular dynamics. The number of studies of surface properties has, however, been relatively small. One of the reasons for this is that it has been difficult to observe spectra of small amounts of adsorbate in heterogeneous systems. Modern spectrometers are sufficiently sensitive to overcome this problem and may readily be used to measure relaxation times, line widths and chemical shifts of adsorbate nuclei. The study of chemical shifts may give information on the structure of the adsorbate, the variation of line widths and relaxation times together give information on the microscopic dynamic properties of the adsorbate. Riehl and Fisher reported relaxation measurements for  $H_2$  adsorbed on graphite [9].

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# Metal Catalyzed Olefin Epoxidation Using Hydroperoxides

Bruce Cook

Literature Seminar

November 18, 1982

## Introduction

The use of complexes of Group IVB, VB and VIB metals as catalysts in the epoxidation of olefins using organic hydroperoxides has achieved wide industrial application. The report by Indictor and Brill [1] in 1965 of the epoxidation of olefins using catalytic amounts of soluble Mo, V, and Cr complexes and tert-butyl hydroperoxide precipitated much of the industrial application. Today the Halcon process as a source of propylene oxide generates over three million tons of product and a billion dollars in sales a year.

A myriad of complexes [3,4] can catalyze these epoxidations, but complexes of molybdenum such as  $\text{Mo}(\text{CO})_6$  and  $\text{MoO}_2(\text{acac})_2$  have the widest application because of their high selectivity and reactivity [5]. The complexes of V(V) such as  $\text{VO}(\text{acac})_2$  also are of particular interest because of their unusual selectivity for the epoxidation of allylic alcohols [6].

## Mechanistic Aspects

Sheldon in 1974 isolated the same Mo(VI) complex from both the  $\text{Mo}(\text{CO})_6$  and  $\text{MoO}_2(\text{acac})_2$  catalyzed reaction mixtures. He postulated that Mo(VI) and the respective highest oxidation states of V, W, Ti and Cr were the true catalytic species due to oxidation by hydroperoxide, and that these probably contain an oxometal functional group. He then rationalized the relative activities of the various metal complexes on the basis of how good a Lewis acid their respective metal oxides are.



Mimoun [7] in 1970 reported the synthesis of  $\text{Mo}(\text{O}_2)_2\text{OL}_2$  by reacting  $\text{MoO}_3$ , ligand (L), and  $\text{H}_2\text{O}_2$ . This complex was found to selectively epoxidize 2 equivalents of olefin, and he proposed it as a possible intermediate in the organic hydroperoxide epoxidations. The general rate law for the reaction is shown in equation (1) which led Mimoun

$$-\frac{d[\text{Mo}(\text{O}_2)_2\text{OL}_2]}{dt} = \frac{a[\text{Mo}(\text{O}_2)_2\text{OL}_2][\text{Olefin}]}{b + c[\text{Olefin}]} \quad (1)$$

to conclude that the olefin is involved in competition with the ligand for a coordination site on the molybdenum. He also proposed the formation of a 5-member 1,3-dipolar cyclic intermediate in the formation of the epoxide. Arakawa and Ozaki [8] were able to isolate an analogous  $\text{Mo}(\text{O}_2)_2\text{O}$  complex from a reaction mixture composed of  $\text{MoO}_3$ , t-BuOOH, and HMPA in dichloroethane by quenching the reaction mixture with bipyridine. Sharpless, et al. [9], were unable to isolate any such intermediate from an analogous benzene solution; however, they did not use bipyridine as a quenching agent. Sharpless [10] reported  $^{18}\text{O}$  labeling studies and the relative rates of norbornene:cyclohexene

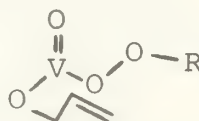


for  $\text{Mo}(\text{O}_2)_2\text{OL}_2$  and several systems with known cyclic transition state sizes, the results of which he contends are more consistent with a three-center transition state rather than the 5-member transition state proposed by Mimoun.

Sharpless, et al. [9], reported an  $^{18}\text{O}$  study of the reaction of tert-butyl hydroperoxide of two different olefins catalyzed by  $\text{MoO}_2(\text{acac})_2$  and  $\text{VO}(\text{acac})_2$ . These labeling studies were inconsistent with a  $\text{Mo}(\text{O}_2)_2\text{O}$  type intermediate. They proposed an alternative intact hydroperoxide with coordination most likely occurring through the hydroxy oxygen (Structure I). The specificity of V(V) for allylic



I



II

alcohols was explained by the formation of a vanadate ester intermediate (Structure II). Sheldon [11] has explained the isolation of the  $\text{Mo}(\text{O}_2)_2\text{O}$  species by Arakawa and Ozaki by a pH dependence of the catalytic species, with the bis-peroxo species being observed in significant concentration only in basic solutions. Mimoun [12] has proposed a new catalytic cycle incorporating the intact coordinated hydroperoxide but maintaining olefin coordination and the 5-member cyclic intermediate.

### Applications

Milhelich, et al. [13,14], have used the Sharpless model of a vanadate ester intermediate and simple steric considerations to predict product selectivities for various acyclic homoallylic alcohols. Sharpless and coworkers [15,16] have been able to generate assymmetric epoxidations of olefinic alcohols in extremely high optical purity using titanium tartrate complexes and t-BuOOH.

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## Transition Metal Activation of Carbon-Hydrogen Bonds

Jennifer Holmgren

Literature Seminar

November 23, 1982

The cleavage of carbon-hydrogen (C-H) bonds is a crucial step in the functionalization of saturated hydrocarbons [1]. Such functionalization processes are employed in the conversion of crude oil and coal into more readily utilized fuels. Heterogeneous catalysts currently used to catalyze C-H bond scission reactions require high temperatures and are often not sufficiently selective [2]. Due to the increased product selectivity observed with homogeneous transition metal catalysts [3], their potential use in C-H bond activation has received increased interest in recent years.

### Intramolecular Activation

The first example of homogeneously promoted activation was reported by Kleinman in 1963 [1b]. In this case the mechanism of the C-H bond scission is assisted by bringing the bond into close contact with a metal center. This occurs if the hydrocarbon group is part of a ligand which is precoordinated to the metal [4]. These reactions are termed "cyclometallations" or "orthometallations".

### Intermolecular Activation

Intermolecular C-H bond activation is less common than intramolecular activation. In the presence of  $\text{PtCl}_4^{2-}$  salts, simple alkanes catalytically undergo deuterium exchange in  $\text{D}_2\text{O}/\text{CH}_3\text{CO}_2\text{D}/\text{DCl}$  at  $100^\circ\text{C}$  [5]. Though this example dates to 1969, further progress in this area has been made only recently. This progress was prompted by the realization that an unsaturated metal center facilitates reaction with the alkane [3].  $\text{IrH}_2(\text{Me}_2\text{CO})_2(\text{PPh}_3)_2^+$  [6] and  $\text{L}_2\text{ReH}_7$  ( $\text{L} = (\text{p-F-C}_6\text{H}_4)_3\text{P}$ ,  $\text{PPh}_3$ ,  $(\text{p-MeC}_6\text{H}_4)_3\text{P}$ ,  $\text{PEt}_2\text{Ph}$ ) [7] can dehydrogenate cyclic alkanes with the aid of 3,3-dimethyl-1-butene as a hydrogen acceptor. Similarly  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{PMe}_3)\text{H}_2$  [8] and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})_2$  [9] add free alkanes. In the latter two cases [8,9], the intermediate hydridoalkyl metal species has been isolated. These systems [6-9] are stoichiometric, not catalytic.

### Clean Metal Surface Studies

Since metal surfaces display enhanced C-H bond activation, it is believed that homogeneous systems which mimic active surface sites are more likely to lead to useful homogeneous catalysts [6b]. For example, "steps" and "kinks" on surfaces have been shown to be more active than "terrace" sites [10,11]. These sites differ from the bulk metal in that they are less coordinatively saturated and possess asymmetric orbital arrays [11].

C-H bond cleavage on a metal surface may occur via a 3-center-2-electron bond [10]. Models for such systems exist in transition metal chemistry [12]. Perhaps a deeper understanding of heterogeneous catalysts can be obtained through such modelling of metal surfaces.



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# Synthesis and Reactivity of $\mu_3$ -Alkylidyne Triosmium Cluster Compounds

Debra S. Strickland

Final Seminar

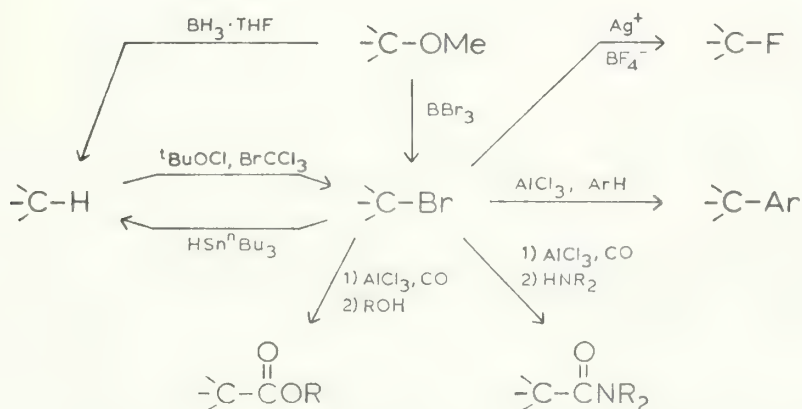
January 27, 1983

The need to develop alternatives to oil as our major source of fuel and chemical feedstock is prompting a re-examination of the mechanisms of the Fischer-Tropsch synthesis reaction [1]. This synthesis converts hydrogen and carbon monoxide, available from coal, into mixtures of hydrocarbons, olefins, and oxygenated compounds, and is catalyzed by metal and metal oxide surfaces. Little is known about the mechanisms which lead to the various products but recent studies have shown that the first step can be dissociative chemisorption of carbon monoxide to give reactive surface carbon atoms [2]. In order to design new, selective catalyst systems an understanding of the key mechanistic steps is crucial.

The complexity of the catalytic systems and the difficulties inherent in examining surface reactions has led some investigators to mimic possible surface reactions with soluble organometal clusters which, because of their multimetal sites, present attractive models for the structures and reactivities of small molecules chemisorbed to a metal surface [3]. The recent synthesis of several clusters with exposed carbon atoms [4,5] suggests that the reactivity of a cluster carbon atom will increase as its coordination number decreases.

Methods have been developed for the functionalization of the triosmium carbon unit at the carbon atom and the reactions imply the intermediacy of carbocationic and carbon radical cluster carbides. The reactivity of three carbonylmethylidyne clusters,  $\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CCO})$  and the related, and more reactive, acylium cation and acyl radical species, was investigated. Also examined were reactions which involve hydrogen migration from metal sites to alkylidyne carbon atoms.

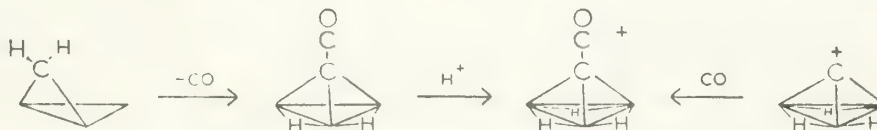
The synthetically useful routes for the interconversion of  $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CY})$  clusters are outlined below. The only previously known clusters in this group were those with  $\text{Y}=\text{H}$  [6],  $\text{CH}_3$  [7], and  $\text{OCH}_3$  [8].



The bromomethylidyne cluster is reactive with Lewis acids as is the analogous  $\text{Co}_3(\text{CO})_9(\mu_3\text{-CCl})$  [9]. Notably, the triosmium carbocation can be generated with  $\text{AgBF}_4$  and is reactive enough to abstract

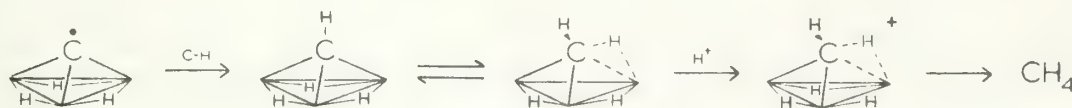


fluoride from the counterion, and to add to CO to give an acylium cation. The acylium is also available by protonation of  $\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CCO})$ , which is the unexpected product obtained from thermolysis of  $\text{Os}_3(\text{CO})_{11}\text{CH}_2$  [10]. Hydrogenation of  $\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CCO})$  yields  $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})$ , demonstrating that the C-C coupling process is reversible. Nucleophiles attack  $\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-CCO})$  at the methylidyne carbonyl carbon atom and the CCO ligand can be reduced to  $\text{CCH}_2$  with  $\text{BH}_3 \cdot \text{THF}$ .



The triosmium carbon radical,  $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-C}\cdot)$ , can be generated under mild conditions from  $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CBr})$  with photochemically-produced  $\cdot\text{Re}(\text{CO})_5$  radicals. This method has permitted an exploration of the chemistry of this unusual carbide cluster, a chemistry which includes hydrogen abstraction from hydrocarbon C-H bonds and addition to aromatic rings. When generated in  $d^{12}$ -cyclohexane under CO, both the deuterium-substituted cluster and a bisalkylidyne diketone, which results from initial addition of CO to the cluster carbon radical, are isolated.

Slow intramolecular H/D exchange in  $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CD})$  takes place at  $25^\circ\text{C}$ . Similar metal-to-carbon hydrogen migration processes are observed for  $\mu_3$ -alkylidyne clusters in which an apical organic CO moiety can coordinate to a metal center, allowing isolation of the alkylidene isomers. Loss of methane from the methylidyne cluster is facilitated by protonation, and anion coordination has produced triosmium clusters with tridentate sulfate and phosphate ligands.



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## Inorganic Applications of Polarization Transfer NMR

Kurt S. Rothenberger

Literature Seminar

February 11, 1983

Polarization transfer in NMR spectroscopy is a process by which the magnetization of one nuclear species, S (usually protons) is transferred to another nuclear species, I, through a scalar coupling,  $J_{IS}$ . This results in a signal enhancement of the I nuclei by  $\gamma_S/\gamma_I$ , where  $\gamma$  is the gyromagnetic ratio.

Several methods of bringing about polarization transfer have been put forth [1]. One of the most popular and successful methods thus far is called "Insensitive Nuclei Enhanced by Polarization Transfer" (INEPT). This pulse sequence was first proposed by Morris and Freeman [2] and can be described as follows:

S:  $(\pi/2)_X - \tau - (\pi)_X - \tau - (\pi/2)_{y,-y}$   
 I:  $(\pi) - \tau - (\pi/2) - \text{acquire}$

In addition to the signal gain due to population transfer, a savings in spectrometer time also results, since the rate at which the sequence can be repeated depends on the usually short proton relaxation times, rather than those of the I nucleus. The sequence yields a spectrum with peak ratios distorted from their expected binomial distribution, as can be seen in Figure 1b. If, however, a waiting period,  $\Delta$ , is introduced following the final pulses, the peak phases will change relative to each other, which allows normal decoupling procedures to be employed [3], and selective enhancement of I nuclei with specific multiplicities (e.g., CH carbons) [4].

Polarization transfer enhancement has been found to persist in the presence of paramagnetic relaxation agents, whereas nuclear Overhauser enhancement does not. This makes it an effective tool for recording C-13 NMR of paramagnetic transition metal complexes [5]. The technique has been applied to simple Sn-119 and Si-29 compounds by Doddrell, Pegg, Brooks, and Bendall [6]. Experimentally determined enhancement factors compared well with those predicted by theory for a nucleus coupled to many protons [7]. Helmer and West [8] have reported enhancement factors of 2.9 to 9.3 for a wide variety of Si-29 spectra with Si-H couplings of up to three bonds. Some very impressive examples of Ag-109 and Rh-103 NMR spectra have been published by Brevard, van Stein, and van Koten [9]. Time saving factors were estimated at up to 400 for Ag-109 and 900 for Rh-103. Brevard and Schimpf have demonstrated INEPT results by transferring magnetization from P-31 instead of protons, to coordination complexes of Rh-103, W-183 and Fe-57 containing phosphine ligands [10].

In mid-1982 an alternative to the INEPT pulse sequence was proposed by Doddrell, Pegg, and Bendall [10]. The technique, "Distortionless Enhancement by Polarization Transfer" (DEPT), provides the same theoretical enhancement as does INEPT, but with multiplets in their "undistorted" binomial distribution. An example



is shown in Figure 1c. The basic DEPT pulse sequence is:

S:  $(\pi/2)_Y - 1/2J - (\pi)_Y - 1/2J - (\theta)_{X,-X} - 1/2J - \text{decouple}$   
 I:  $(\pi/2)_Y - 1/2J - (\pi)_{X,-X} - 1/2J - \text{acquire}$

The variable length  $\theta$  pulse has the same functional form as does the waiting period,  $\Delta$ , in INEPT and determines what coupling multiplicities will be enhanced. The DEPT sequence has been applied to Si-29 and Pt-195 with enhancement factors slightly less than those obtained with INEPT [12]. This is attributed to  $T_2$  relaxation of the I nucleus during the longer time needed for the DEPT sequence. A commercially available routine, "Automatic DEPT" (ADEPT) can sample a C-13 spectrum at four different values of  $\theta$  and, using appropriate combinations, generate subspectra of only CH, CH<sub>2</sub>, or CH<sub>3</sub> carbons [13].

Though recently developed, these techniques have already been shown effective on a multitude of compounds of interest to the inorganic chemist. The techniques are straightforward in operation and require no special instruments or modifications. Their recent commercial availability could be an indication of widespread future use in NMR.

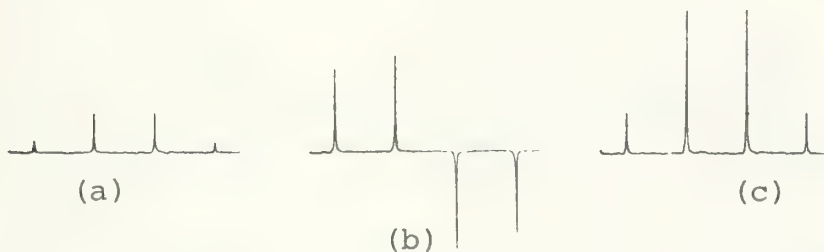


Figure 1: (a) Normal FT; (b) INEPT; and (c) DEPT C-13 NMR spectra of the methyl carbon in acetic acid.

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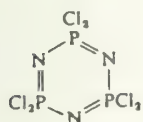
## Cyclophosphazene Chemistry

David J. Maltbie

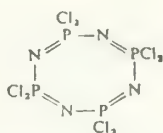
Literature Seminar

February 24, 1983

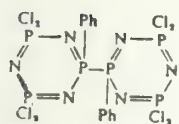
Cyclophosphazenes are heteroatom ring compounds which contain the repeating unit  $-(N=PRR')-$ , where R and R' can be halogens, amino groups or organic radicals. The first cyclophosphazene to be reported was the cyclic trimer,  $(PNCl_2)_3$  (a). Its preparation was described in 1834 by Liebig and Wohler, making cyclophosphazenes one of the earliest known inorganic heterocyclic compounds [1]. Many other structural types have been reported including the cyclic tetramer (b), the bridged dimer (c), and a fused ring tricyclic compound (d) [1]. The synthesis of an interesting compound having a closed structure and phosphazene character,  $K_6[P_{12}S_{12}N_{14}]$ , was described by Fluck in 1976 [2]. This molecule consists of 12 fused 6-membered rings containing both divalent and trivalent nitrogen atoms (e).

 $P_3N_3Cl_6$  ( trimer)

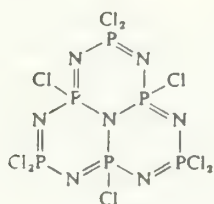
(a)

 $P_4N_4Cl_8$  ( tetramer)

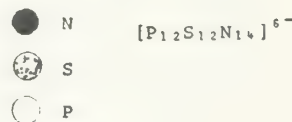
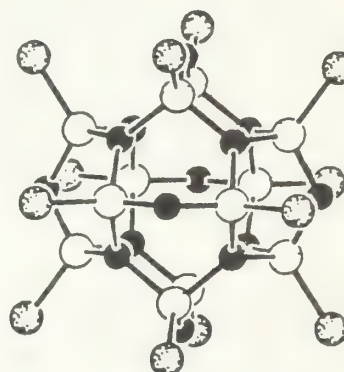
(b)

 $P_6N_6Cl_6(C_6H_5)_2$ 

(c)

 $P_6N_7Cl_9$ 

(d)

 $[P_{12}S_{12}N_{14}]^{6-}$ 

(e)

The simple cyclic phosphazenes can be made in a very complex reaction between  $NH_4Cl$  and  $PCl_5$  [1]. The mechanism of this reaction has been carefully studied by several workers [3]. The trimer can be extracted from the product mixture with acid, but separation of the other cyclic products is difficult. The synthesis of the bridged dimer is straightforward as it is a major product of the reaction between the trimer and methyl or phenyl magnesium chloride in THF [4]. No direct route has been reported for the synthesis of  $P_6N_7Cl_9$ . It can be made in low yield from polymerization then depolymerization of a mixture of low molecular weight cyclophosphazenes [5]. The  $P_{12}S_{12}N_{14}$  anion is more cooperative and forms in good yield when  $P_4S_{10}$  is added to molten KSCN [2].



The chemistry of the trimer has been extensively investigated [6]. It undergoes aminolysis, hydrolysis, and metathetical exchange reactions. The trimer also reacts with alkoxides, aryl oxides, and thiolates to form a variety of products including spirocyclic compounds [7]. Some of these spirocyclic cyclophosphazenes form molecular inclusion compounds with small organic molecules [8]. Several cyclophosphazene complexes have been reported which contain transition metals bound to the trimer [9], tetramer [10], and the hexamer [11]. Coordination to the metal can occur at the ring phosphorus [9] or nitrogen atom, or using ring and exocyclic nitrogen atoms [10]. Another interesting complex reported by Allcock contains an icosahedral carborane unit bound to the trimer through a phosphorus-carbon bond [12]. Recently, Allcock and Harris have explored the reaction of the trimer with carbanions [13]. Allcock has proposed a metal-halogen exchange mechanism to explain the interaction of the trimer with organocuprate complexes. The chemistry of the higher order cyclophosphazenes ( $[NPX_2]_n$  where  $n=4-8$ ) has not been investigated as thoroughly, but they appear to undergo some of the same reactions as the trimer [6]. The bridged dimer reacts with sodium alkoxides and aryl oxides to give substituted bicycloposphazenes and monomers [14]. The chemistry of  $P_6N_7Cl_9$  is very limited as substitution of the chlorines for more electron withdrawing groups causes collapse of the trimeric structure [5]. However, dimethylamine reacts to form an octakisdimethylamine derivative in which only one of the bonds to the central nitrogen is cleaved. The reaction chemistry of the  $P_{12}S_{12}N_{14}$  anion has not been reported, this may be due to low solubility in organic solvents.

The trimer is essentially a planar ring when it is symmetrically substituted having substituents extending above and below the plane [15]. The tetramer and the higher rings have different conformations in solid state depending on their substituents [16,17], but the  $^{31}P$  NMR spectrum in solution usually shows the phosphorus atoms to be equivalent for symmetrically substituted derivatives [18]. The structure of  $P_6N_7Cl_9$  is interesting as the rings are made up of two almost planar segments, one containing the trivalent central nitrogen, the other bent down from the central plane at a  $25^\circ$  angle [5]. The 6-membered rings in  $P_{12}S_{12}N_{14}^{6-}$  are even more contorted due to the presence of two trivalent nitrogen atoms in each ring, and the restriction of forming a closed structure [2]. The structure of the  $P_{12}S_{12}N_{14}$  anion, which has  $T_h$  symmetry, can best be visualized by looking at the various closed geometric figures it contains. The triply bridging nitrogen atoms form a cube, the doubly bridging nitrogen atoms are arranged in an octahedron, and the sulfur atoms describe a slightly distorted icosahedron. Finally, the phosphorus and triply bridging nitrogen atoms are at the vertices of a pentagonal dodecahedron.



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## Alkylidene Dirhodium Chemistry

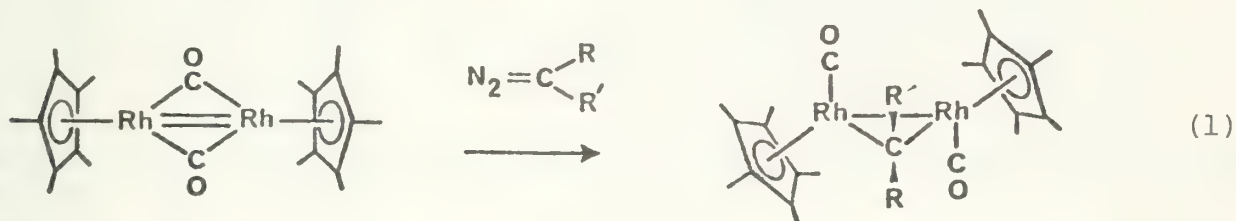
Peter A. Dimas

Final Seminar

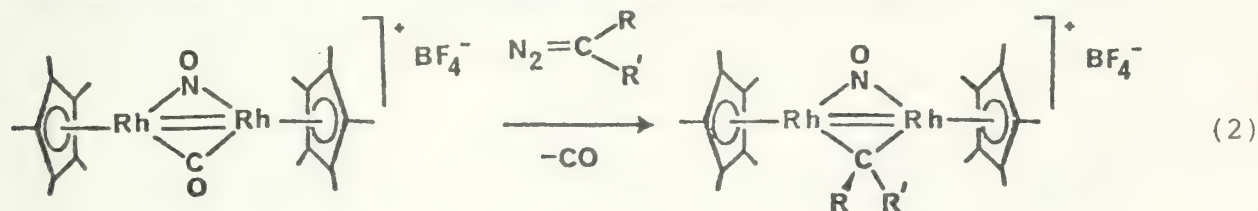
February 25, 1983

The synthesis and study of transition metal complexes of new carbon-containing ligands constitute continuing objectives of organometallic chemists. In recent years, dimetal and cluster complexes containing the alkylidene bridge,  $\mu\text{-CRR}'$ , have attracted considerable attention [1]. This is due, in part, to the implicated role of alkylidene intermediates in surface processes such as the chemisorption of hydrocarbons [2] and the hydrogenation of carbon monoxide [3]. The number of molecular  $\mu$ -alkylidene complexes has proliferated in a relatively short period of time. Current efforts are focused on examining the reactivity of these complexes.

We have found that unsaturated dirhodium compounds react with diazoalkanes to give  $\mu$ -alkylidene compounds. This synthetic approach, which is analogous to the cyclopropanation reaction of organic chemistry, is based on the isolobal relationships between metal-metal double bonds and alkenes. Thus  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-CO})]_2$  reacts rapidly with diazo compounds at room temperature to form  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\text{CO})_2(\mu\text{-CRR}')]_2$  quantitatively. Thermolysis of one member of this set results in decarbonylation to form an unsaturated compound (see reaction 1) [4].

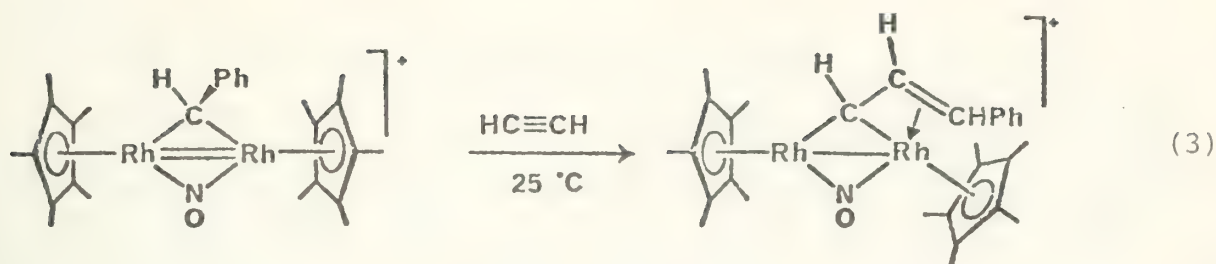


Another unsaturated complex,  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-NO})(\mu\text{-CO})]\text{BF}_4$ , has been prepared from  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2]$  and  $\text{NOBF}_4$ . It also reacts with diazo compounds ( $-78^\circ\text{C}$ ) to form  $\mu$ -alkylidene complexes which decarbonylate upon warming to room temperature resulting in a novel series of unsaturated  $\mu$ -alkylidene compounds (reaction 2) [5].

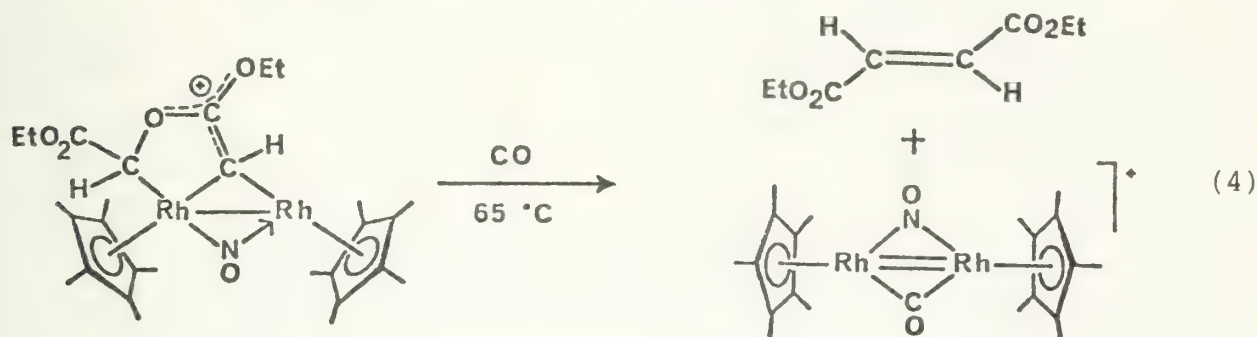


These compounds provide us with a unique opportunity to examine the reactivity of alkylidene groups toward unsaturated hydrocarbon ligands under milder conditions than previously possible.  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-NO})(\mu\text{-CHPh})]\text{BF}_4$  is highly reactive toward acetylene, forming a stable vinylmethylidene compound via alkyne insertion into the metal-alkylidene bonds (reaction 3).



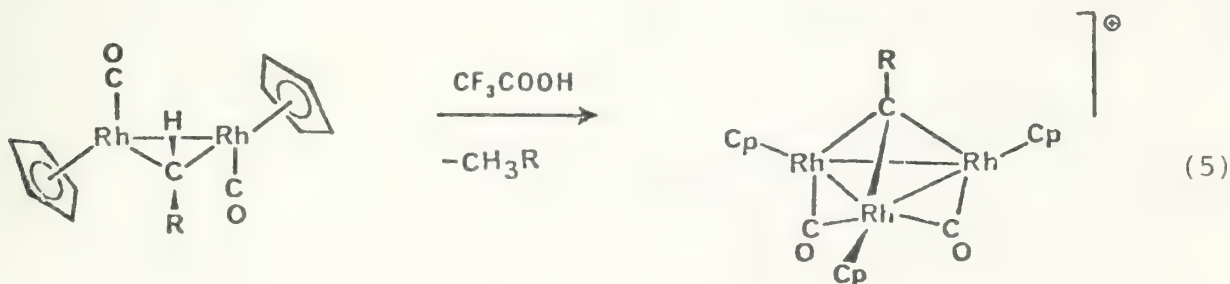


A bis-alkylidene complex has been prepared from  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{-Rh}_2(\mu\text{-NO})(\mu\text{-CO})]\text{BF}_4$  and ethyl diazoacetate. The two alkylidene moieties are condensed into a unique dimetallocycle, resulting in a bridging alkylidene moiety and a terminal one. Heating a solution of this dimetallocycle under a carbon monoxide atmosphere induces coupling of the alkylidene moieties to form an alkene (reaction 4).



Crossover experiments provide evidence for an intramolecular coupling mechanism [6].

An important aspect of the reactivity of alkylidene groups on metal surfaces is their interconversions with alkyl or alkylidyne groups. In order to generate molecular analogs of these transformations we have examined the protonation of several  $\mu$ -alkylidene complexes. Treatment of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\mu\text{-CHR})]$  ( $\text{R} = \text{H}, \text{Me}$ ) with trifluoroacetic acid causes disproportionation to give  $\text{CH}_3\text{R}$  and the novel cationic alkylidyne clusters  $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Rh}_3(\mu\text{-CO})_2-(\mu_3\text{-CR})]^+$  (reaction 5) [7].





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## Polyiminoalanes

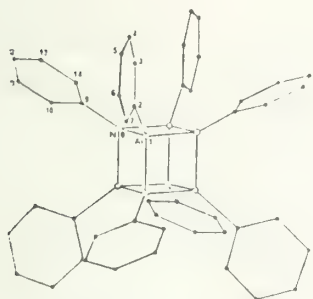
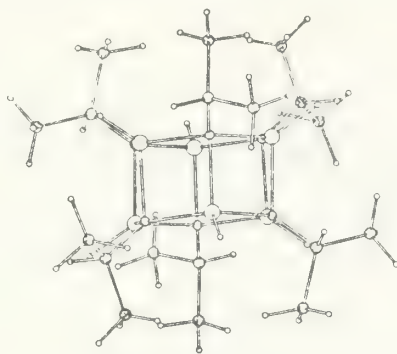
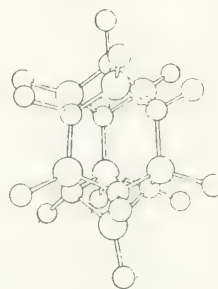
Curtis Schwartz

Literature Seminar

March 1, 1983

Compounds having the composition  $(\text{RAlNR}')_n$  ( $\text{R}=\text{alkyl, halogen, H; R}'=\text{alkyl}$ ) are known as polyiminoalanes (PIA). Early information concerning the structures of PIA's were indefinite since the PIA's isolated were either insoluble polymers or slightly soluble crystalline polymers which were studied by infra-red spectroscopy, cryoscopy, mass spectrometry, elemental analysis, and x-ray powder diffraction [1-3]. The first structural characterization of a PIA was reported in 1962 on crystalline  $(\text{C}_6\text{H}_5\text{AlNC}_6\text{H}_5)_4$  made by reaction of aniline and hexaphenyldialuminum in refluxing benzene [4]. Its structure was shown by single crystal x-ray diffraction to consist of a cubic cage of alternating aluminum and nitrogen atoms with phenyl substituents filling the fourth coordination position around each aluminum and nitrogen atom. Since this discovery, new soluble PIA's have been prepared in crystalline form for  $n=4-8$ , and their structures elucidated by single crystal x-ray diffraction [5-9].

All of the basic cage structures adopted by PIA's from  $n=4-8$  are made up of 4 and/or 6 membered rings of alternating aluminum and nitrogen atoms in different ring conformations. For the compound  $(\text{HAlN-iso-C}_3\text{H}_7)_6$ , the cage is found to be that of a hexagonal prism made up of a nearly planar 4 and 6 membered rings, whereas for  $(\text{CH}_3\text{AlNCH}_3)_7$ , the cage is made up of a total of 5 six membered rings, three of which are in the boat and two in the chair conformations. The molecule  $[(\text{HAlN-iso-C}_3\text{H}_7)_2(\text{H}_2\text{AlNH-iso-C}_3\text{H}_7)_3]$  contains a 6 membered ring in the skew boat conformation.

 $(\text{C}_6\text{H}_5\text{AlNC}_6\text{H}_5)_4$  $(\text{HAlN-iso-C}_3\text{H}_7)_6$  $(\text{CH}_3\text{AlNCH}_3)_7$ 

Several approaches have been utilized for the synthesis of PIA's [10,11], which may be isolated as moisture sensitive crystals from ether or hydrocarbon solvents from the following chemical reactions:

1.  $\text{RNH}_2 + \text{AlR}'_3 \longrightarrow \frac{1}{n}(\text{R}'\text{AlNR})_n + 2\text{R}'\text{H}$
2.  $\text{RNH}_2 + \text{MAlH}_4 \longrightarrow \frac{1}{n}(\text{HAlNR})_n + \text{MH} + 2\text{H}_2 \quad \text{M}=\text{Li, Na}$
3.  $\text{Al} + \text{RNH}_2 \xrightarrow{\text{H}_2} \frac{1}{n}(\text{HAlNR})_n + \frac{1}{2}\text{H}_2$



The degree of polymerization and product distribution are strongly dependent on the conditions under which the synthesis is carried out as well as the type of amine. Isopropyl, *n*-propyl, and *t*-butyl amine have yielded PIA's of principally a single degree of polymerization. With *t*-butyl amine, PIA's of  $n=4$  are preferred, whereas with isopropyl, cyclohexyl, and sec-butyl amine, the hexameric  $n=6$  PIA's are preferred. PIA's made from ethyl or *n*-butyl amine give mixtures of oligomers which are difficult to separate.

Since the cage structures of PIA's can be shown to be derived from 4 and 6 membered heterocyclic rings of aluminum and nitrogen atoms, hypotheses may be formulated concerning the mechanism of cage formation. Reaction intermediates in the synthesis of PIA's from equation 3 have been characterized spectroscopically and a reaction sequence suggested [11]. A reaction intermediate in the synthesis of  $(\text{CH}_3\text{AlNCH}_3)_7$  has been isolated and characterized by x-ray diffraction. However, it is not clear how the reaction intermediate collapses to the PIA product in this particular case [12].

PIA's are reactive molecules. The hydrogen atoms bound to aluminum may be substituted with alkyl substituents [13,14] or chlorine [15] without cage decomposition by several routes. The aluminum hydride fragment may also be completely replaced by a Ca or Mg atom coordinated to 3 and 1 THF solvent molecules, respectively [16,17]. Other derivatives of PIA's are also known [18-21].

It has been found that PIA's exhibit very high activity as hydrogenation cocatalysts with organotransition metal complexes [22]. PIA's have also been used effectively as cocatalysts with  $\text{TiCl}_4$  in the polymerization of *cis*-polyisoprene [23].

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# Selective Oxidation and Ammoxidation of Propylene by Bismuth Molybdate Catalysts

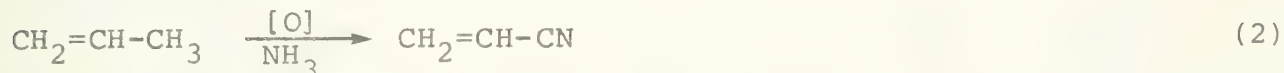
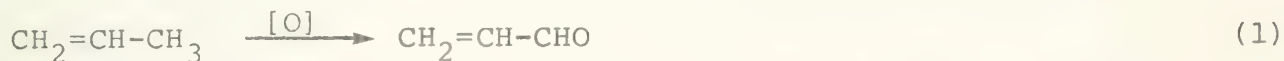
Ren-Chain Wang

Literature Seminar

March 17, 1983

## Introduction

Bismuth molybdates catalyzing selective oxidation (1) and ammoxidation (2) of propylene were discovered and developed at Sohio [1,2] in the early 1960's.

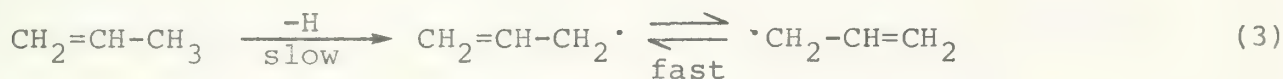


Since then, many fundamental studies have employed catalysts containing different bismuth to molybdenum atomic ratios. As a result of such studies, it is now known that bismuth molybdate catalysts display high activity and selectivity only if their Bi/Mo compositions lie within the range of 2/3 to 2/1 [3].

Depending on conditions such as the initial Bi/Mo ratio, pH value, reaction temperature, and interaction time, three major products can be isolated by co-precipitation from a mixed solution of bismuth nitrate and ammonium molybdate. The products are  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$  (2.3,  $\alpha$ ),  $\text{Bi}_2\text{Mo}_2\text{O}_9$  (1:1,  $\beta$ ) and  $\text{Bi}_2\text{MoO}_6$  (2:1,  $\gamma$ ) [4-7]. The structures  $\alpha$ ,  $\beta$  and  $\gamma$  differ in a number of ways: (1) the number of oxygens bound only to Bi (from 0 to 2); (2) the degree of clustering of  $\text{MoO}_4$  (from 2 to layered); and (3) the number of  $\text{Bi}^{3+}$  vacancies (from 1 to 0) [8].

## Mechanism

In a series of experiments using deuterium-labeled propylenes, Adams and Jennings [9] established the rate-determining nature of the  $\alpha$ -hydrogen abstraction, in which a first order deuterium isotope effect ( $k_H/k_D = 1.82$ ,  $T = 450^\circ\text{C}$ ) was observed. By studying the isotopic distributions of the oxidation products of  $^{14}\text{C}$ - and  $^{13}\text{C}$ -labeled propylenes, Sachtler [10] and McCain [11] concluded that equation (3) is the key step in the selective oxidation (ammoxidation)

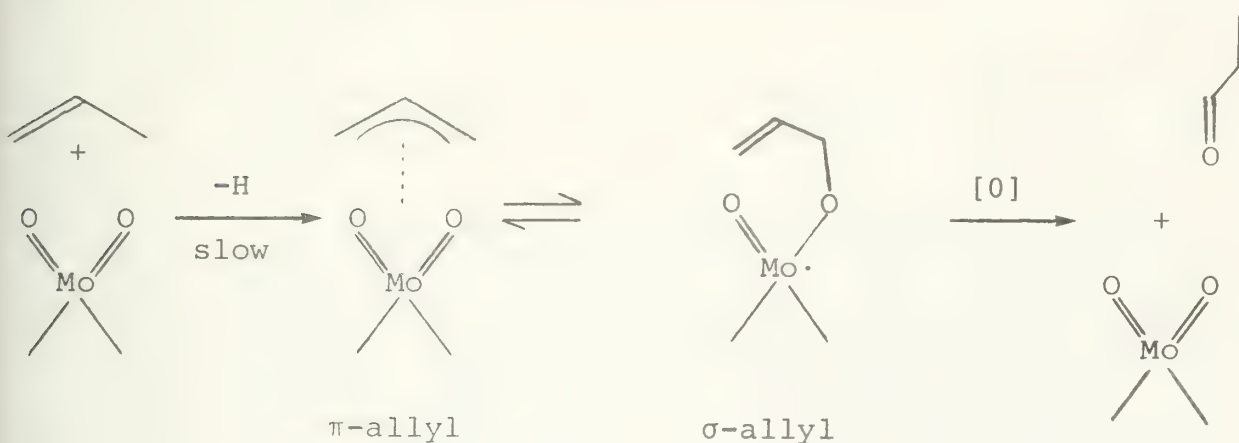


Grzybowska and Haber [12] in 1977 suggested that reactions with bismuth molybdate catalysts proceed via the association of allyl radicals with oxygens bound to bismuth. A number of factors led them to this conclusion. The isomerization of propylene to

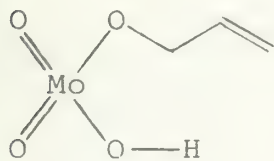


1,5-hexadiene and benzene occurs only with  $\text{Bi}_2\text{O}_3$ . Additionally, molybdenum polyhedra are oxygen inserters, and acrolein is known to be formed from the reaction of  $\text{MoO}_3$  with "allyl radical" (from thermally decomposed allyl iodide). These experiments introduced the important multi-center (dual-site) concept [13], though there are still many different postulates about the roles of bismuth and molybdenum in  $\alpha$ -H abstraction and olefin adsorption [12-15].

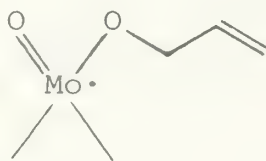
By comparing the product distributions of the reaction of azopropene over  $\text{MoO}_3$ , the reaction of allyl iodide over  $\text{MoO}_3$ , and the reaction of propylene over bismuth molybdates, Burrington and Grasselli [16] concluded that the general reaction route is:



In order to shed light on the details of the selective oxidation (ammoxidation) mechanism, in 1980 Grasselli and Burrington [15] studied the selective oxidation of  $\text{d}_0$ , 1,1- $\text{d}_2$  and 3,3- $\text{d}_2$  allyl alcohol over  $\text{MoO}_3$  and  $\text{Bi}_2\text{O}_3 \cdot n\text{MoO}_3$  ( $n=0, 1, 3$ ). From the product distributions and their similarities with the distributions obtained from analogous reactions with the well-studied  $\text{Mo(VI)}$  ester (I) [17] and  $\text{Mo(V)}$  ester (II) (which may be an intermediate in the selective oxidation of propylene), they proposed a more complete mechanism [15] for the selective oxidation (ammoxidation) of propylene over Bi-Mo catalysts.



(I)



(II)



## Redox properties

Brazdil and Grasselli [18] utilized a pulse microreactor method to reduce the catalysts with propylene in the absence of oxygen and subsequently to reoxidize the partially reduced catalysts by gaseous oxygen. They found that the unit area rates of lattice oxygen participation decrease in the order:  $\text{Bi}_2\text{Mo}_2\text{O}_9 > \text{Bi}_2\text{Mo}_3\text{O}_{12} > \text{Bi}_2\text{MoO}_6$  and the reoxidation rates decrease in the order:  $\text{Bi}_2\text{MoO}_6 > \text{Bi}_2\text{Mo}_2\text{O}_9 > \text{Bi}_2\text{Mo}_3\text{O}_{12}$ . They also found that the maximum selective utilization of reactive lattice oxygen occurs after partial reduction for  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$  and  $\text{Bi}_2\text{Mo}_2\text{O}_9$ . These results are consistent with a selective oxidation mechanism requiring coordinatively unsaturated metal ions in complex shear domains.

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## Platinblau: Recent Structural Studies

Susan L. Kaiser

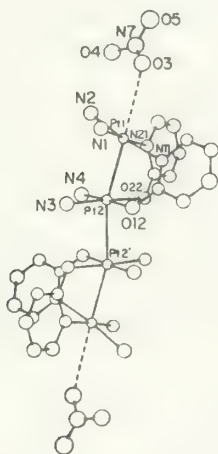
Literature Seminar

April 5, 1983

In contrast to the yellow or colorless nature of most platinum complexes, some ligands yield intense blue or purple complexes that are referred to as platinum blues or platinblau. These blue complexes are not only interesting because of their intense color but also intriguing chemically.

Comparative studies suggest that all known blue compounds are mixed-valent, metal-metal bonded, amidate-bridged oligomers [1]. The chemistry and structures of these complexes, the first of which was prepared by Hofmann and Bugge in 1908 [2], are still not clear and several hypotheses have been reported concerning the mechanism of their function on reaction of platinum(II) complexes with organic ligands such as  $\text{CH}_3\text{CN}$ , uracil, etc. [3]. The discovery that platinum blues (e.g., platinum pyrimidine blues) possess a high index of antitumor activity with a lower associated toxicity than the parent drug,  $\text{cis}-(\text{NH}_3)_2\text{PtCl}_2$  [4], stimulated efforts to characterize them. These platinum blues have also been used as cytologic stains for DNA in electron microscopy [5].

To date only  $\text{cis}$ -diammineplatinum  $\alpha$ -pyridone blue (PPB) has been fully characterized structurally [6]. It consists of four platinum atoms bridged by  $\alpha$ -pyridonate ligands. The tetramer is composed of two centrosymmetrically related dimers, as required by the space group symmetry. This structure determination was a step toward the understanding of the chemistry of platinum blues.



| <u>Distance</u>         | <u>Å</u>    |
|-------------------------|-------------|
| Pt1····Pt2              | 2.779       |
| Pt2····Pt2'             | 2.885       |
| Pt-NH <sub>3</sub> (av) | 2.06        |
| Pt-N(pyridone)          | 2.05        |
| Pt-O(av)                | 2.04        |
| <u>Angle</u>            | <u>Deg.</u> |
| Pt1-Pt2-Pt2'            | 164.5°      |

Spectroscopic and synthetic studies on the platinum pyrimidine blues, etc., show that the solution chemistry of platinum blues is very complicated, with more than one oligomeric platinum species usually existing in solution. Attempts to crystallize other blue complexes have been largely unsuccessful due to their heterogeneous



oligomeric nature. Attention has been drawn to the non-blue structural analogues of the platinum blues in hopes of rationalizing the structures of many blue complexes by analogy. Several non-blue crystalline products have been isolated from reaction mixtures that ultimately produce cis-diammineplatinum pyrimidine blues even though crystals of the blue product have not to date been obtained [7-10]. Three structures of non-blue compounds obtained in the reaction of cis-diammineplatinum(II) with  $\alpha$ -pyridone were reported [11]. These analogues contain one, two or four platinum atoms. Often these derivatives are "head-to-head" or "head-to-tail" dimers, or tetranuclear platinum complexes. An example of a "head-to-head" arrangement for a platinum dimer bridged by two ligands is where one platinum is bound to a nitrogen from each ligand and the other platinum is bound to an oxygen from each ligand. Conversely, the "head-to-tail" arrangement is where each platinum is bound to one nitrogen and one oxygen.

cis-Diammineplatinum  $\alpha$ -pyrrolidone tan was obtained from the reaction of the cis-diammineplatinum(II) hydrolysis product with  $\alpha$ -pyrrolidone [12]. It is interesting to note that the platinum oxidation state in cis-diammineplatinum  $\alpha$ -pyridone is 2.25, whereas in cis-diammineplatinum  $\alpha$ -pyrrolidone tan it is 2.5 [12].

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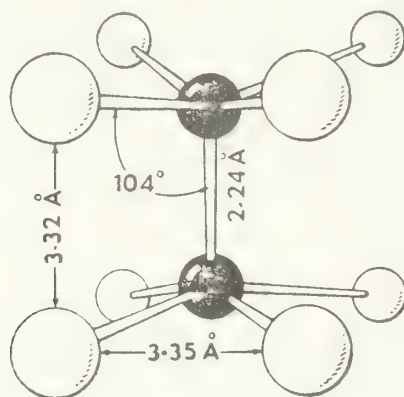
# Quadruple Bonds in Group VI Metal Complexes

Deborah Main

Literature Seminar

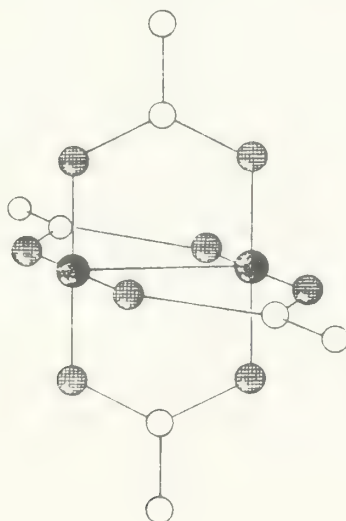
April 7, 1983

Although the first discovery of a compound containing a quadruple bond can be traced back as far as 1844 when Eugene Peligot first synthesized  $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ , it was not until 1964 that quadruple bonds were recognized to exist. This recognition came when the structure of  $\text{KReCl}_4 \cdot \text{H}_2\text{O}$  was reported to contain the dimeric unit  $[\text{Re}_2\text{Cl}_8]^{2-}$  (1) [1]. The bonding and electronic structure of  $[\text{Re}_2\text{Cl}_8]^{2-}$  was interpreted in terms of a quadruple bond consisting of one  $\sigma$ -, two  $\pi$ -, and one  $\delta$ -component between the rhenium atoms. Since then, the chemistry surrounding this important class of coordination complexes has developed very rapidly [2-6].



1

Today, there are five elements known to participate in quadruple bonding, three of which belong to Group VIB, namely, chromium, molybdenum, and tungsten. Of the quadruply bonded compounds known, the carboxylate complexes,  $\text{M}_2(\text{O}_2\text{CR})_4$  (2) are probably regarded as the single most important class because they have traditionally been the starting materials for the synthesis of almost all other derivatives (except for the case of  $\text{M}=\text{W}$ ).



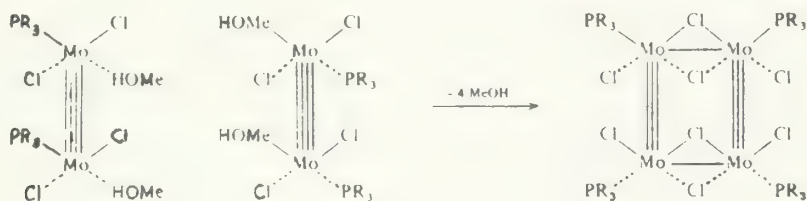
2



Peligot's original synthesis of  $\text{Cr}(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$  involving addition of  $\text{NaO}_2\text{CCH}_3$  to an aqueous solution of  $\text{Cr}^{2+}$  is still one of the easiest and most efficient means of preparing  $\text{Cr}_2(\text{O}_2\text{CR})_4$  compounds [7], although new methods have been introduced [8]. The molybdenum carboxylates can be prepared by heating  $\text{Mo}(\text{CO})_6$  with carboxylic acid in various solvents such as diglyme, toluene, and 1,2-dichlorobenzene [9] or by reduction of  $\text{MoO}_3$  [10]. However, preparation of the tungsten analogs,  $\text{W}_2(\text{O}_2\text{CR})_4$ , have been extraordinarily elusive, as have  $\text{W}_2^{4+}$  compounds in general. Only recently has success been reported with the preparation of  $\text{W}_2(\text{O}_2\text{CCF}_3)_4$  [11].  $\text{W}_2\text{Cl}_8(\text{THF})_4$  is reduced to  $\text{W}_2\text{Cl}_4(\text{THF})_4$  with two equivalents of sodium amalgam at  $-20^\circ\text{C}$  followed by addition of sodium trifluoroacetate and subsequent workup.

The rapid growth of compounds containing quadruple M-M bonds can largely be attributed to the desire to produce new compounds with bridging ligands which are stereoelectronically similar to the carboxylates. Research in this area has led to the discovery of certain ligands which yield "supershort" M-M bonds [12-14]. Examples of compounds containing such ligands include  $\text{Cr}_2(2,6-(\text{OCH}_3)_2\text{C}_6\text{H}_3)_4$  ( $\text{Cr}-\text{Cr} = 1.847 \text{ \AA}$ ),  $\text{Cr}_2-(\text{CH}_2\text{NC}(\text{Ph})\text{NCH}_2)_4$  ( $\text{Cr}-\text{Cr} = 1.843 \text{ \AA}$ ),  $\text{Cr}_2((\text{CH}_2)_2\text{P}(\text{CH}_3)_2)_4$  ( $\text{Cr}-\text{Cr} = 1.895 \text{ \AA}$ ), and the compound containing the shortest known M-M bond,  $\text{Cr}_2(2-\text{OCH}_3-5-\text{CH}_3\text{C}_6\text{H}_3)_4$  ( $\text{Cr}-\text{Cr} = 1.828 \text{ \AA}$ ). The factors responsible for such shortness in the Cr-Cr bond have been investigated but are presently unknown.

Dinuclear quadruply bonded complexes undergo a variety of reactions: oxidative addition, reductive elimination, Lewis base association and dissociation, and insertion-deinsertion reactions. Recent work by McCarley and co-workers has led to perhaps the most intriguing of all reactions, namely, the dimerization of two such species to give tetranuclear complexes (Scheme 1) [15].  $\text{Mo}_4\text{Cl}_8(\text{PEt}_3)_4$  was the first such compound prepared and structurally characterized. It was found to contain a rectangular array of metal atoms with alternating single-triple metal-metal bonds [15]. Since then, several new tetranuclear compounds have been synthesized [16-18].



Scheme 1



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## The Controversy Surrounding the Structure of Zeolite A

Philip J. Koerner, Jr. Literature Seminar

April 8, 1983

### Introduction

Zeolites are crystalline, microporous aluminosilicates consisting of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra linked via common oxygen atoms. Enough cations are present to neutralize the anionic framework. There are over 100 structures known for natural and synthetic zeolites. Synthetic zeolites have been used extensively in industry over the past 25 years. The three major uses are: as adsorbents [1,2], in ion exchange [1,3], and in catalysis [2,3].

The first reported synthesis of zeolite A was in 1956. Its basic building block is the sodalite unit, or truncated octahedron. The sodalite unit is a 24-vertex polyhedron, with Si and Al atoms at each vertex, having 14 faces: 6 square and 8 hexagonal. Each sodalite unit is linked to six others through the square faces. This octahedral arrangement of sodalite units leads to three types of cavities in zeolite A: square prisms, the sodalite cavities, and the larger supercages. Access to the supercage, with a diameter of 11.4 Å, is gained through one of the six windows (so called 8-rings) having a diameter of 4.2 Å [1,2].

Zeolite A is normally prepared with Na as the cation, however it can be ion exchanged by treatment with an aqueous solution of a new cation. The three most common forms of zeolite A are: 3A (K form), 4A (Na form), and 5A (Ca form).

### The Positions of Exchangeable Cations

The preparation of zeolite 4A was first reported by Breck and his coworkers at Union Carbide [4]. Subsequent x-ray diffraction studies yielded small data sets for hydrated and dehydrated 4A [5,6]. Seff redetermined the crystal structure of dehydrated 4A and assigned eight  $\text{Na}^+$  ions to positions near the centers of the 6-rings, three  $\text{Na}^+$  ions near the centers of 8-rings and the twelfth  $\text{Na}^+$  to a position in the supercage normal to a 4-ring [7]. In other crystal structure studies of various ion exchanged forms of zeolite A Seff reported "zero-coordinate"  $\text{Rb}^+$ ,  $\text{K}^+$ , and  $\text{Na}^+$  [8], and near zero-coordinate  $\text{Cs}^+$  [9],  $\text{Tl}^+$  [10],  $\text{Ca}^{2+}$ , and  $\text{Sr}^{2+}$  [11]. A cation was defined as "zero-coordinate" if the distance between the cation and all other atoms exceeded the sum of their ionic radii by more than 1.0 Å [12].

Due to skepticism about the zero-coordinate ions raised by the lack of elemental analysis and the use of the pseudocell (Pm3m) instead of the true unit cell (Fm3c), Smith began to redetermine the structure of dehydrated zeolite A containing supposed zero-coordinate cations. His studies have shown no evidence for zero-coordinate  $\text{K}^+$  [13] and  $\text{Na}^+$  [14]. He has also found that the near zero-coordinate  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  cations are really  $\text{K}^+$  ions scavenged during the ion exchange process [15,16].



## Ordering of the Aluminosilicate Framework

Smith was able to refine the superstructure and differentiate between Si-O and Al-O bonds. The average Si-O distance of 1.60 Å and Al-O distance of 1.73 Å [13,14] are in excellent agreement with the pure Si-O and Al-O distances of 1.61 and 1.75 Å for feldspar minerals [17]. The Si/Al ratio of 1.0 in zeolite A should lead to a strict alternation of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra according to Loewenstein's rule, which forbids Al atoms from sharing neighboring tetrahedral sites [18]. The comparison of <sup>29</sup>Si magic angle spinning NMR (MASNMR) spectra for various aluminosilicates seemed to provide evidence for Si bonded to 3 Al and 1 Si via O bridges (the so-called Si(3 Al) or 3:1 model) and vice versa [19], a bonding mode which violates Loewenstein's rule. However, a more recent <sup>29</sup>Si MASNMR study of ZK-4, a highly siliceous, synthetic zeolite isostructural with zeolite A, provided evidence for the Si(4 Al) (4:0) model, which is in agreement with Loewenstein's rule [20,21].

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## Application of Conversion Electron Mössbauer Spectroscopy to Surface Studies

Seung-Mo Oh

Literature Seminar

April 12, 1983

The majority of Mössbauer spectroscopic experiments are performed in a transmission geometry and measure the resonant absorption of a thin absorber. In this mode, data relating to the bulk properties of solids may be obtained.

However, there has been a significant interest in the past few years in backscattering techniques, mainly based on the detection of conversion electrons emitted after resonant events [1,2]. Because these conversion electrons are attenuated rapidly in matter, only those electrons produced in regions close to the surface can escape and the resulting Mössbauer spectrum is weighted towards the surface regions of the absorber. Thus, Conversion Electron Mössbauer Spectroscopy (CEMS) is useful for the analysis of the surface properties of the sample.

Two basic types of CEMS experiments may be performed. The first of these involves the detection of the total flux of backscattered electrons (Integral CEMS), while in the other type, the flux of scattered electrons is energy-resolved and Mössbauer spectra are accumulated using selected bands of electron energy. The latter technique allows the surface regions of solid to be probed as a function of depth (Depth-selective CEMS, DCEMS).

Comprehensive theoretical studies on the intensity and energy distribution of scattered electrons were made using Monte Carlo methods by Liljequist, et al. [3,4].

The ability of DCEMS to probe the surface regions of solids of small surface area in situ (in a non-destructive manner) has made the method particularly suitable for the examination of technical problems such as corrosion [5,6], surface treatment [7] and phase changes [8]. Keune and Sette Camara [5] have studied the oxidation of iron foils at high temperature, and fully demonstrated the ability of this technique to identify new phases formed at surfaces. A very thin surface layer of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, an intermediate layer of Fe<sub>3</sub>O<sub>4</sub>, followed by a thick layer of FeO were all identified as oxidation products.

Recently, the application of CEMS to rather diverse iron-containing materials has been expanding. Some examples include studies on solid phase reactions [9], thin films [10], single crystals [11], minerals [12] and hydrogen storage compounds (e.g., FeTi [13,14]).



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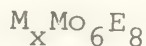
## Chevrel Phases

Dean Giolando

Literature Seminar

April 26, 1983

First synthesized [1] by Chevrel in 1971 [2], the Chevrel phases are a series of solid solution compounds characterized by the general formula



where M is a metallic element and E the chalcogenides. The fundamental structural unit is the cluster  $Mo_6 E_8$  [3]. This building block has the same geometry and stoichiometry as the  $M_6 X_8^{n+}$  unit in a number of early transition metal halides [4] (Figure 1).

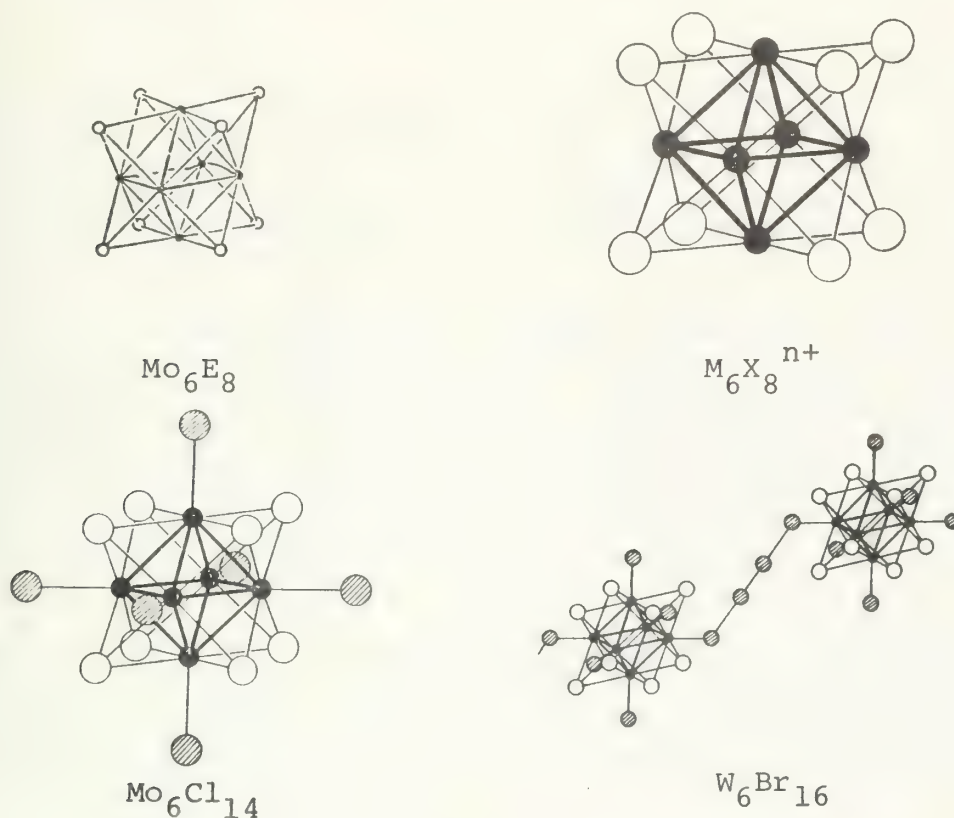


Figure 1

The halogenides can occur as discrete molecules,  $MoCl_2$ , or separated by additional ligands,  $W_6Br_{16}$ . However, the chalcogenides consist of  $Mo_6 E_8$  clusters contacted through intercluster Mo-Mo and Mo-E interactions [3,5,6]. The compounds,  $M_x Mo_6 E_8$  crystallize in a rhombohedral-hexagonal structure having a rhombohedral unit cell with  $\alpha \sim 90^\circ$ .

This arrangement of the  $Mo_6 E_8$  units results in cavities in the chalcogenide network. These cavities are filled by the element M and consist of two types. The first, generally occupied by large elements, is located at the origin with an approximately cubic environment of chalcogenides. The second type is circularly delocalized about the origin in 12 pseudo-tetrahedral sites (Figure 2).







Figure 2

Generally, these compounds are prepared directly [2,7,8,9] from the elements at temperatures in excess of 1000°C, or from the metal chalcogenide. The binary phases,  $\text{Mo}_6\text{Se}_8$  and  $\text{Mo}_6\text{Te}_8$ , can be prepared by direct syntheses. The  $\text{Mo}_6\text{S}_8$  phase has been found too thermally unstable to be prepared directly but indirect methods were found successful.

To better understand the structural and superconducting properties of these phases, a number of molecular orbital and band structure calculations have been performed [10]. There is general agreement on the overall distribution of the energy levels: there is rough separation of the chalcogen-p states and the Mo d states; an energy gap exists between 12 Mo d states from the remaining Mo d states; and the Fermi level lies within the first, narrow, set of 12 Mo d states. The states of the conduction band correspond to partially filled Mo  $d_{x^2-y^2}$  orbitals.

The Chevrel phases are characterized by their unusual superconducting properties. These properties include high critical temperatures ( $T_C$ ) [11], high upper magnetic field ( $H_{C2}$ ) [12], and, apparently, the coexistence of magnetism and superconductivity [13]. For the Chevrel phases [14],

$$T_C = 10 f_1 f_2 \exp\left(\frac{-1.04(1+\lambda)}{1.9-0.062\lambda}\right).$$

The quantities  $f_1$  and  $f_2$  are correction factors and  $\lambda$  is the electron-phonon interaction.

The high critical fields, up to 600 kG for  $\text{PbMo}_6\text{S}_8$  are due to the particular structural and electronic features of the phases. For a "dirty" superconductor, BCS theory gives [15],

$$H_{C2}^* \sim \frac{T_C}{\xi v_F} \sim \rho N_{BS}(0) T_C \quad \text{or} \quad \left(\frac{dH_{C2}^*}{dT}\right)_{T_C} = 4.4 \times 10^4 \rho \gamma$$



where  $\ell$  is the mean free path,  $\rho$  is the normal state resistivity and  $v_F$  is the Fermi velocity ( $= \frac{1}{\hbar} \frac{dE}{dk}$ ). The last expression predicts a linear relationship between  $\left( \frac{dH}{dT} c_2 \right)_{T_c}$  and the specific heat coefficient,  $\gamma$ .

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## Alkane Activation by Metal Atoms

David Hammerton

Literature Seminar

May 5, 1983

Vaporized metal has been used for over fifty years in industrial concerns for depositing thin metal films on materials ranging from plastics to metal supports [1]. Many studies of metal film deposition date from as early as 1937 [2], but it was not until 1965 that a technology was developed using vaporized atoms as reagents. Skell and Wescott devised a method of synthesis using carbon vapor cocondensed with organic compounds at 77 K [3]. P. L. Timms applied this technique to metals [4]. His use of inorganic and organic substrates helped establish metal vapor chemistry as a viable synthetic technique [5].

In metal vapor synthesis, highly reactive atoms or molecules are generated at a high temperature in vacuum and are brought together (cocondensed) with vaporized coreactants onto a cold surface [6]. Generally the coreactant to metal ratio is 10:1 to 100:1. Pressure requirements are  $10^{-3}$  to  $10^{-4}$  torr and the cold surface temperature can range from 10-273 K although 77-195 K is a more typical range.

Many transition metals have been used in metal vapor synthesis. To date nearly all transition metals have been tried [7]. Although each metal has a different reactivity, they all tend to aggregate if the cold surface temperature becomes too high.

Two main areas of research have developed since the first metal atom/alkane matrix experiment was reported. One area concerns single and di-atom insertion into carbon-hydrogen and carbon-carbon bonds in alkanes. The other involves metal aggregation and its effect on alkane matrices.

In 1977, Ozin, et al., monitored the optical spectra of vanadium and divanadium in alkane matrices [8]. Although no direct interaction between the vanadium and the alkane matrix was seen, the nature of the alkane matrix did affect the optical spectrum. The following year, two metal insertions were reported. Barrett, et al., found evidence of what was thought to be diiron insertion into the carbon-hydrogen bond of methane [9]. Skell, et al., cocondensed zirconium atoms with various alkanes and found direct evidence of carbon-carbon and carbon-hydrogen bond insertion [10].

Photolysis has been used in conjunction with metal vapor synthesis by Billups, et al., to effect insertion of iron atoms into a carbon-hydrogen bond in methane [11] and by Ozin and coworkers to insert copper atoms into methane and ethane carbon-hydrogen bonds [12,13]. Photolysis has also been used to remove iron atoms from a carbon-iron-hydrogen bond in  $\text{HFeCH}_3$  [14].

M. L. H. Green and coworkers used metal vapor synthesis to insert molybdenum atoms into carbon-carbon bonds of spiro-[2,4]hepta-4,6-diene [15]. Using this reaction as a model, Green oxidatively added molybdenum atoms to carbon-carbon bonds in hexamethylcyclo-





pentadiene [16] and reacted tungsten atoms with spiro-[2,4]hepta-4,6-diene [17]. The tungsten moiety proved to have a rich chemistry and many derivatives of this compound were synthesized. Recently, Green reported an unusual Ti/ $\beta$ -carbon interaction that provided insights into carbon-carbon and carbon-hydrogen bond activation [17].

In 1976, Klabunde and coworkers studied nickel and magnesium atom aggregation in alkane matrices [18]. Cluster formation was monitored between 77 K and 143 K. Both aggregates were then warmed to room temperature, dried under vacuum, and investigated for catalytic activity. The nickel aggregate proved to be an efficient hydrogenation catalyst while the magnesium aggregate was useful as a Grignard reagent. At the time of this investigation, Klabunde had assumed that the alkane species were physis- and chemisorbed onto the nickel clusters. Upon reinvestigation, Davis and Klabunde found evidence for carbon-carbon bond cleavage of the alkane matrix below 143 K [19]. Klabunde and coworkers continued their investigation of nickel aggregation in various solvents [20]. The catalytic activity of the nickel powders produced from these reactions was studied. They found nickel-pentane and nickel-hexane powders to be very active hydrogenation catalysts for benzene, 1-butene, 1-heptene and butadiene. Nickel-toluene powders were also active catalysts for selective hydrogenation of 1,3-butadiene to 1- and 2-butene. Nickel-THF powders were found to be fairly inactive as hydrogenation or olefin isomerization catalysts. In 1981, Klabunde, *et al.*, reported a detailed analysis of several nickel-alkene powders [21]. The magnetic and chemical properties of the powders were reported. Various amounts of carbon were incorporated into these small crystallites (<35 Å) depending upon preparative conditions.

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## Organometallic Chemistry of Tungsten-Triosmium Cluster Compounds

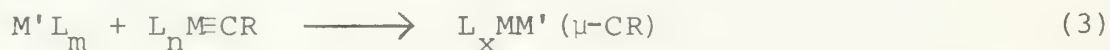
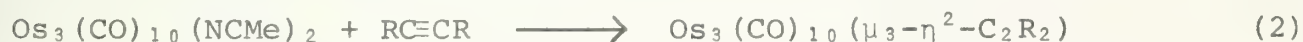
Joon T. Park

Final Seminar

June 23, 1983

The chemistry of transition metal cluster compounds has emerged over the last decade as one of the most rapidly expanding areas of organometallic chemistry [1]. This is in part due to a prospect that discrete cluster molecules may mimic metal surfaces in the processes of chemisorption and catalysis. Currently, mixed metal cluster compounds are under intense scrutiny since they have a number of advantages over their homonuclear counterparts [2]. The present study involves the synthesis, structure, and reactivity of several new tungsten-triosmium ( $\text{WOs}_3$ ) cluster compounds. The presence of a tungsten atom in the cluster framework imparts a considerably different reactivity pattern than that observed in triosmium chemistry.

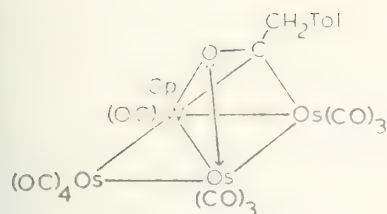
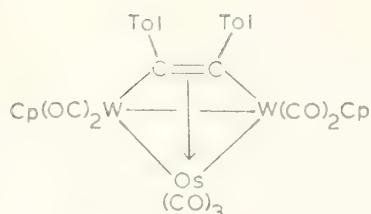
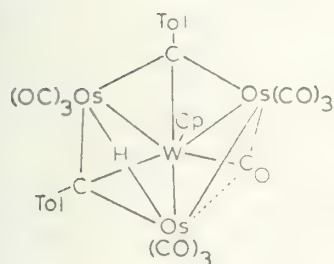
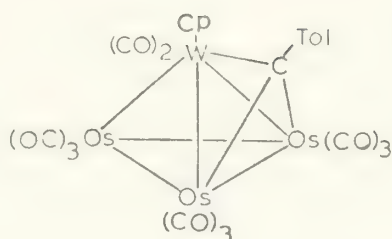
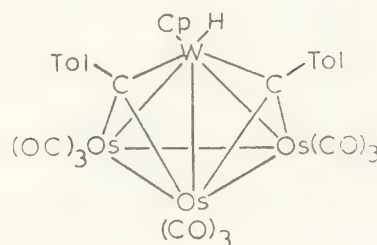
Since the unsaturated osmium cluster  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  and the "lightly stabilized" osmium complex  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$  were reported, their reaction chemistry has been extensively examined. In particular, it has been shown that  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  undergoes facile insertion reactions with many alkynes ( $\text{RC}\equiv\text{CR}$ ) to form alkenyl derivatives [3] (equation (1)), while  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$  also reacts with alkynes to provide alkyne triosmium complexes [4] (equation (2)). Stone and coworkers have utilized the isolobal relationships between alkynes and metal alkylidyne complexes ( $\text{L}_n\text{M}\equiv\text{CR}$ ) to prepare a series of mixed-metal  $\mu$ -alkylidyne species [5] (equation (3)). The success of this idea has prompted a study of the two reactive triosmium clusters with a tungsten alkylidyne to form  $\text{WOs}_3$  cluster compounds.



In contrast to the reaction with alkynes, however, a remarkably facile Os-Os bond cleavage has been observed in the reaction of  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  with  $\text{Cp}(\text{CO})_2\text{W}\equiv\text{CTol}$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ,  $\text{Tol} = p\text{-C}_6\text{H}_4\text{Me}$ ), giving three products by three parallel pathways:  $\text{CpWOs}_3(\text{CO})_{11}(\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol})$  (1),  $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_7(\mu_3\text{-}\eta^2\text{-C}_2\text{Tol}_2)$  (2), and  $\text{CpWOs}_3(\text{CO})_{10}(\mu_3\text{-CTol})_2\text{H}$  (3) [6]. Interestingly, the reaction of  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$  with  $\text{Cp}(\text{CO})_2\text{W}\equiv\text{CTol}$  gave a major product,  $\text{CpWOs}_3(\text{CO})_{11}(\mu_3\text{-CTol})$  (4), in which the  $\text{Os}_3$  skeleton remains intact.





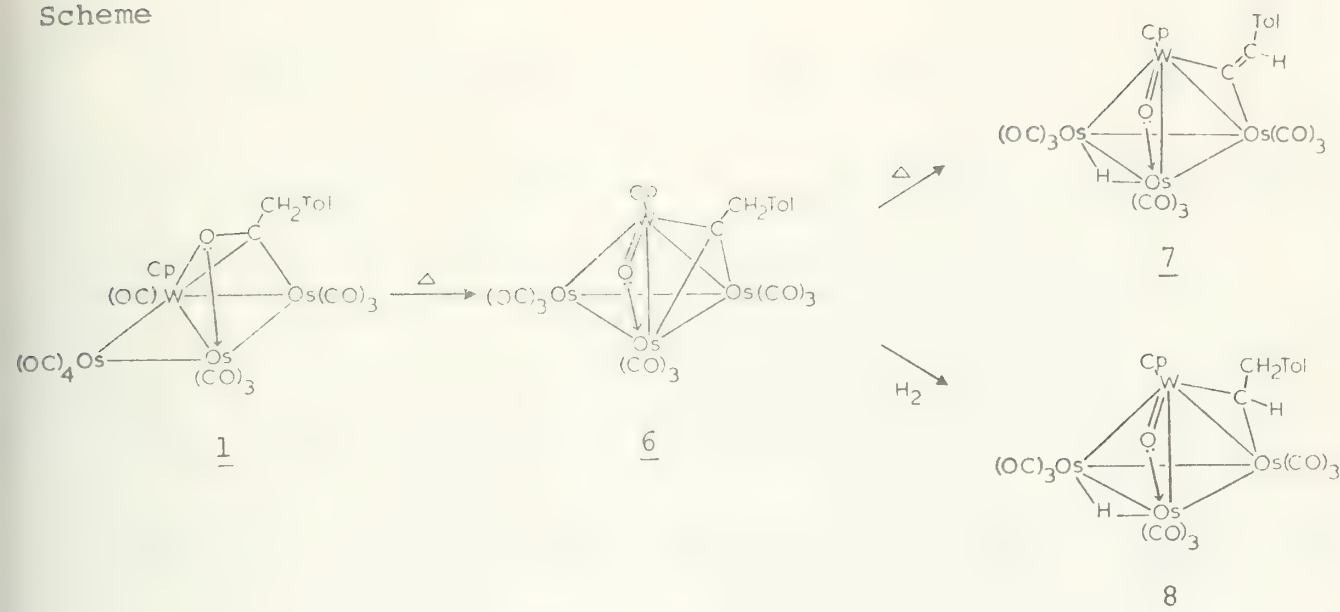
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Compound 1 is the only product derived from a 1:1 combination of the reactants. The second major product 2 has been shown to crystallize with two isomers in a single crystal by Churchill and co-workers [7]. Variable-temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the third product 3 show that it undergoes a degenerate framework rearrangement that interchanges the two inequivalent  $\mu_3\text{-CTol}$  groups. This is interpreted as breaking and making hydrogen-bridged metal-metal bonds. In addition, the dialkylidyne compound 3 cleanly transforms to a new symmetrical dialkylidyne complex,  $\text{CpWOs}_3(\text{CO})_9(\mu_3\text{-CTol})_2\text{H}$  (5), by loss of a carbonyl ligand in refluxing toluene. Compound 4 is isostructural with the known compounds  $\text{M}_3(\text{CO})_9(\text{C}_2\text{R}_2)$  ( $\text{M} = \text{Fe}$  [8],  $\text{Os}$  [9]). Compounds 2 and 4 have been prepared from different routes and characterized independently by Stone and co-workers [10].

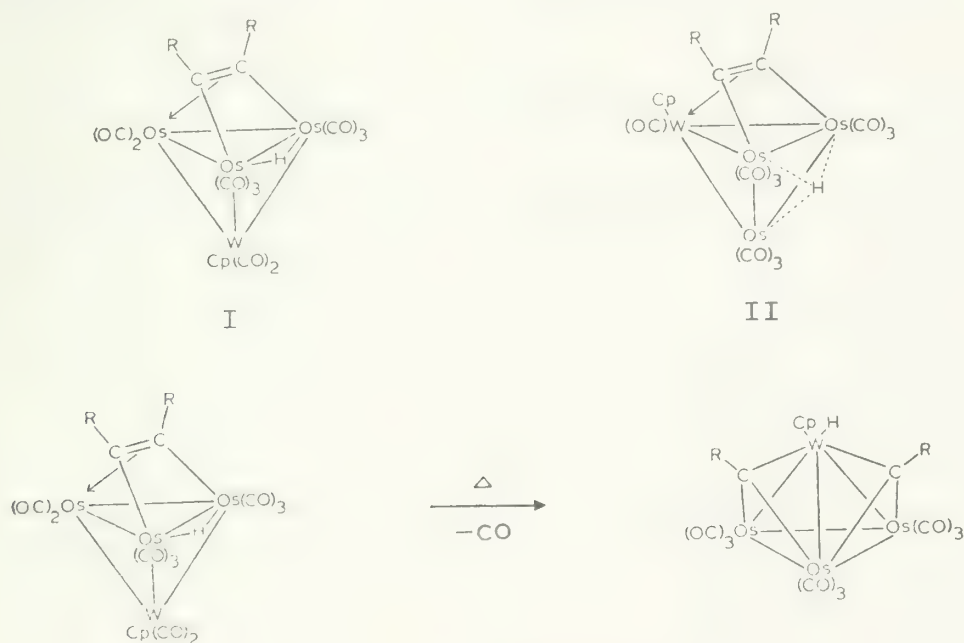
Compound 1,  $\text{CpWOs}_3(\text{CO})_{11}(\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol})$ , undergoes acyl CO bond scission to provide the doubly bridging oxo-alkylidyne compound,  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$  (6) (see Scheme). This CO bond cleavage suggests that the deoxygenation process for reductive oligomerization of carbon monoxide can occur directly from surface acyl species. Compound 6 itself exhibits interesting reactivity such as oxidative addition of a benzylic hydrogen and conversion to a hydrido-alkylidene compound by dihydrogen, yielding  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu\text{-C=CHTol})\text{H}$  (7) and two isomers of  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})\text{H}$  (8), respectively. This reactivity implicates reversible movement of the oxo-ligand from a bridging to terminal position, generating a coordinatively unsaturated species as a reactive intermediate.



## Scheme



Reactions of  $\text{CpWOs}_3(\text{CO})_{12}\text{H}$  with a series of alkynes have resulted in the isolation of two isomeric alkyne derivatives,  $\text{CpWOs}_3(\text{CO})_{10}(\mu_3-\eta^2-\text{C}_2\text{R}_2)\text{H}$  (see I and II below). Some of these complexes ( $\text{R} = \text{CO}_2\text{Et}$ ,  $\text{CF}_3$ ) undergo irreversible thermal isomerization of I to II. Surprisingly, diaryl alkyne complexes (isomer I;  $\text{R} = \text{Ph}$ ,  $\text{Tol}$ ) undergo facile intramolecular  $\text{C}\equiv\text{C}$  bond scission reactions after CO loss to yield the corresponding dialkylidyne derivatives,  $\text{CpWOs}_3(\text{CO})_9(\mu_3-\text{CR})_2\text{H}$  (equation (4)) [11]. Both the alkyne and the dialkylidyne complexes display unique structural features. The presence of the tungsten center seems significant; pyrolysis of  $\text{Os}_3(\text{CO})_{10}(\mu_3-\eta^2-\text{C}_2\text{Ph}_2)$  results simply in CO loss to form the unsaturated species  $\text{Os}_3(\text{CO})_9(\mu_3-\eta^2-\text{C}_2\text{Ph}_2)$  without cleaving the alkyne [9].





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# The Chemistry of o-Formylphenyl Aryl Phosphines: Intramolecular Oxidative Additions to Iridium(I) and Phosphorus(III)

Edith F. Landvatter

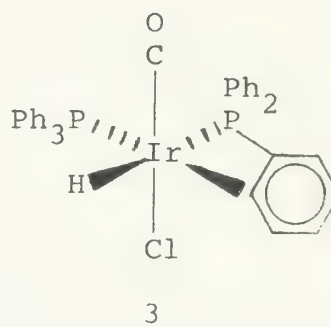
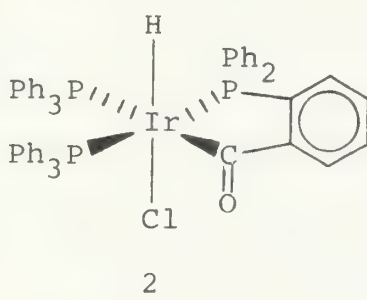
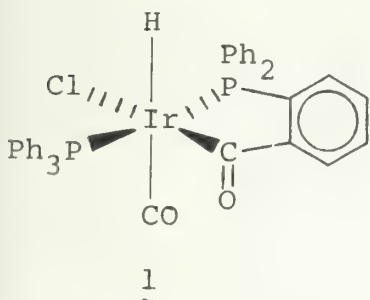
Final Seminar

July 5, 1983

Intramolecular reactions are generally more facile than their intermolecular counterparts. By juxtaposing two functional groups one is often able to accelerate otherwise slow reactions and often trap otherwise unstable intermediates. The present research takes advantage of both of these aspects in probing the interactions of the aldehyde group with low-valent iridium and phosphorus centers. The studies have established new aspects of iridium acyl hydride and organophosphorus chemistry. Additionally, this work revealed some unexpected parallels between the low-valent phosphorus and iridium chemistry.

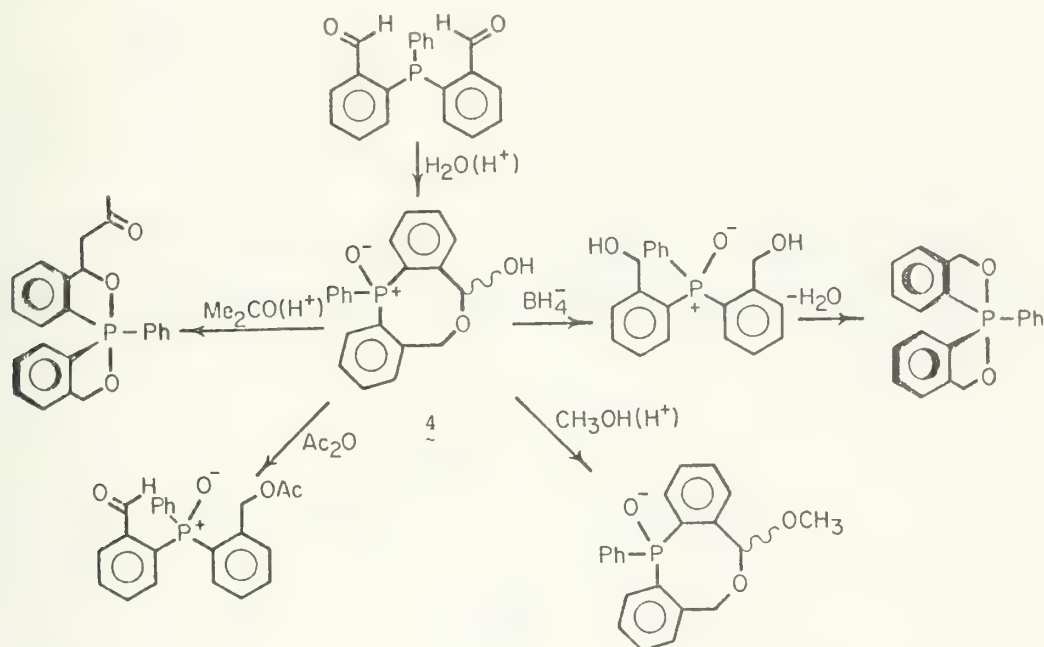
The interaction of aldehydes with transition metals is important in metal catalyzed aldehyde decarbonylation [1] and hydroformylation [2]. Metal acyl hydrides, intermediates often postulated in mechanisms for these transformations, were first obtained by the addition of chelating aldehydes to  $\text{RhCl}(\text{PPh}_3)_3$  [3] and  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  [4].

The addition of  $(\text{o-C}_6\text{H}_4\text{CHO})\text{Ph}_2\text{P}$  (PCHO) to  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  is a highly efficient process which affords acyl hydride 1 [4]. This complex is stabilized by chelation since the nonchelated acyl hydride  $\text{HIr}(\text{PhCO})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  is not obtained either by direct addition of benzaldehyde to  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  or by addition of benzoyl chloride to  $\text{IrH}_3(\text{CO})(\text{PPh}_3)_2$ . The addition of PCHO to  $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$  gives an acyl hydride of configuration 2 as the major product. This tris-phosphine iridium(III) acyl hydride is more labile than 1 and decarbonylation of 2 is more facile than for 1. In the decarbonylation of 2, a steady state concentration of a bis-phosphine carbonyl intermediate was detected by IR and  $^1\text{H}$ -NMR spectroscopy and is proposed to be the orthometallated complex 3.





In the course of our studies on the reactions of iridium with phosphine aldehydes we had occasion to examine the bis-aldehyde phosphine  $(\text{O}-\text{C}_6\text{H}_4\text{CHO})_2\text{PhP}$ . We found that this species undergoes unusual chemistry independent of any metal ions. Thus  $(\text{O}-\text{C}_6\text{H}_4\text{CHO})_2\text{PhP}$  reacts with water to form the hydrate, **4** [6]. The chemistry of this species was studied and its mechanism of formation was elucidated.



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# Thermal and Photochemical Reactivity of Dirhenium Hydrido-Alkenyl Carbonyl Compounds

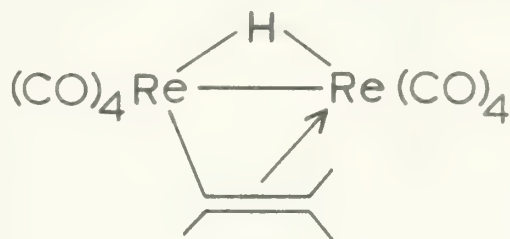
Philip O. Nubel

Final Seminar

August 11, 1983

The photochemistry of  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Re}_2(\text{CO})_{10}$  has been studied extensively within the past several years, particularly with respect to substitution by phosphorus [1] and, to a lesser extent, nitrogen [2] ligands. Substitution has also been effected by thermal means [3] and through the use of  $\text{R}_3\text{NO}$  [4]. Reactions of these compounds with unsaturated hydrocarbons (e.g., olefins and acetylenes) have received much less attention despite potential relevance to catalytic processes such as isomerization, hydrogenation, oligomerization, etc.

UV photolysis of  $\text{Re}_2(\text{CO})_{10}$  at  $25^\circ$  in the presence of ethylene, terminal olefins, or 2-butene results in formation of  $\mu$ -hydrido,  $\mu$ -alkenyl dirhenium octacarbonyl complexes in high yield [5]. The bridging alkenyl ligand forms a  $\sigma$  bond to one Re atom and a  $\pi$  bond to the other.



Analogous to the dirhenium hydrido-alkenyl compounds exist in osmium cluster chemistry; reactions of simple olefins with tri- and tetra-osmium carbonyl compounds yield  $\mu_2$ -hydrido,  $\mu_2$ -alkenyl tri- [6] and tetraosmium [7] products, respectively. In solution, the  $\mu$ -alkenyl ligand of the dirhenium and triosmium complexes undergoes a rapid fluxional process at room temperature in which the  $\sigma$  and  $\pi$  bonds of the alkenyl group are interchanged between the bridged metal atoms [8].

The dirhenium hydrido-alkenyl compounds react with a variety of substrates under mild thermal conditions. Treatment with pyridine,  $\text{P}(\text{OMe})_3$ ,  $\text{PMe}_3$ , or  $\text{P}(\text{OPh})_3$  at  $25^\circ$  results in elimination of olefin and formation of 1,2-eq,eq- $\text{Re}_2(\text{CO})_8\text{L}_2$ . Kinetics investigations of reactions with pyridine are consistent with a mechanism which begins with intramolecular C-H reductive elimination. Treatment with bis(diphenylphosphino)methane (dppm) affords a dppm-bridged complex,  $\text{Re}_2(\text{CO})_8(\text{dppm})$ ; reaction with  $\text{PPh}_3$  or  $\text{P}(\text{n-Bu})_3$  initially generates 1,2-ax,eq- $\text{Re}_2(\text{CO})_8\text{L}_2$  which thermally isomerizes to 1,2-ax,ax- $\text{Re}_2(\text{CO})_8\text{L}_2$ . The hydrido-alkenyl compounds react with ethylene, terminal olefins, or cis- (but not trans-) 2-butene to afford the hydride- and alkenyl-exchanged hydrido-alkenyl species. Treatment with phenylacetylene yields a  $\mu$ -hydrido,  $\mu$ -acetylido dirhenium octacarbonyl complex. Reaction with  $\text{H}_2$  generates  $\text{H}_2\text{Re}_2(\text{CO})_8$ .





Photolysis of  $(\mu\text{-H})(\mu\text{-CH=CH}_2)\text{Re}_2(\text{CO})_8$  in the presence of ethylene affords  $\mu$ -hydrido,  $\mu$ -butenyl dirhenium octacarbonyl complexes. A mechanism is proposed in which the initial step is photo dissociation of CO, inasmuch as photolysis in the presence of  $^{13}\text{CO}$  or  $\text{PPh}_3$  results in CO substitution. Subsequent steps in the formation of the hydrido-butenyl species are coordination of ethylene, insertion of ethylene in the Re-H or Re-ethenyl  $\sigma$  bond, re-coordination of CO, C-C or C-H reductive elimination to yield  $\text{Re}_2(\text{CO})_8(1\text{-butene})$ , and oxidative addition of a vinylic C-H bond of coordinated butene. Slow catalytic production of 1-butene and trans-3-hexene occurs in the photochemical reaction of the hydrido-ethenyl complex with ethylene; butene formation is the result of thermal reaction of the hydrido-butenyl dirhenium species with ethylene, while hexene results from photochemical reaction. Removal of photo dissociated CO from the system via an ethylene-purge during photolysis results in subsequent catalytic production of butene and hexene under thermal (25°) conditions. Photolysis of  $(\mu\text{-H})(\mu\text{-CH=CHCH}_3)\text{Re}_2(\text{CO})_8$  in the presence of propylene yields 2-hexene. A general mechanism for dimerization of olefins is proposed in which a dinuclear metal catalyst effects the insertion of one olefin into a vinylic C-H bond of another. Additionally, cis $\rightarrow$ trans and trans $\rightarrow$ cis isomerization of the bridging alkenyl ligand of  $(\mu\text{-H})(\mu\text{-CH=CHR})\text{Re}_2(\text{CO})_8$  complexes is effected photochemically.

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# An EPR Study of the Myeloma Protein MOPC 315 and the Hybridoma Proteins 29-22 and HPD-1 using a Dnp-Spin Label Hapten

Dean Oester

Final Seminar

August 22, 1983

Cellular and humoral components of the immune response protect the host from invasion by foreign substances referred to as immunogens. Immunoglobulins comprise the humoral response and are high-molecular weight proteins with varying amounts of attached carbohydrate. The basic structural unit of an immunoglobulin consists of two identical, high-molecular weight proteins, heavy (H) chains, and two identical low-molecular weight proteins, light (L) chains [1] (Figure 1). These chains are held together in the immunoglobulin by a varying number of disulfide bonds as well as noncovalent domain interactions based on the characteristic  $\beta$  sheet structure of the protein [2]. Each immunoglobulin unit has two identical active sites.

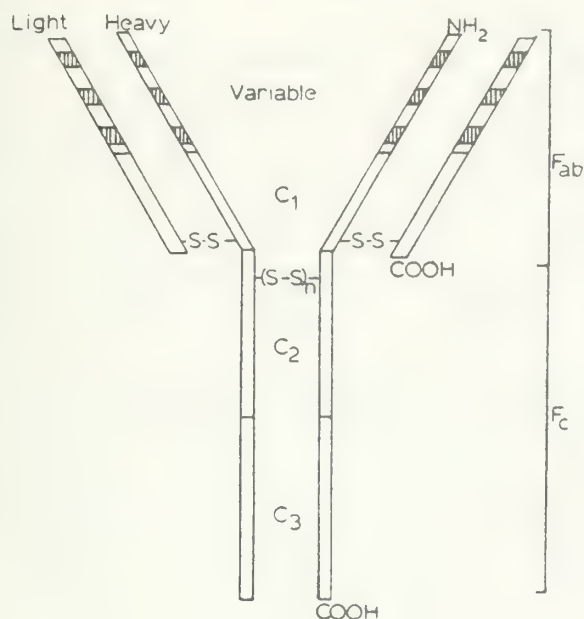


Figure 1

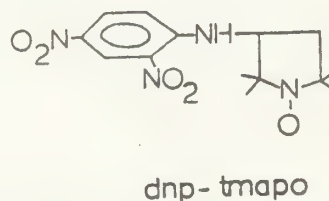


Figure 2

Natural immune responses are characterized by a high degree of heterogeneity with respect to Ig class, affinity toward hapten, and specificity [3]. Affinity is described by the equilibrium between one active site and hapten (Equation 1). The equilibrium constant



increases over time during the immune response. This process is known as maturation with increases in affinity of  $10^7$  observed for some hapten systems [4].

Hsia and Piette pioneered spin label studies on natural heterogeneous immune responses specific to 2,4-dinitrophenyl (Dnp) derivatives. Adducts of Dnp and 2,2,5,5-tetramethylpyrrolidin-1-oxyl at-





tached with varying length hydrocarbon spacers determined the average depth of the active site pocket to be 1.1-1.2 nm [5]. Myeloma proteins, homogeneous immunoglobulins of unknown specificity, were also investigated with this method by Dwek. Based on the degree of anisotropy in the spin label epr spectra, depth as well as lateral dimensions were obtained for the active sites [6].

We questioned the direct correlation of the active site model for Dnp binding to the myeloma MOPC 315 to naturally induced immunoglobulins. Two specifically induced anti-Dnp hybridoma (homogeneous) immunoglobulins, HPD-1 and 29-22, were compared to MOPC 315.

We found the three immunoglobulins to have similar affinities toward Dnp-glycine as measured with fluorescence quenching experiments. The affinity for MOPC 315 was  $1.2 \times 10^5 \text{ M}^{-1}$ , while hybridoma 29-22 had an affinity of  $2.3 \times 10^5 \text{ M}^{-1}$  and hybridoma HPD-1,  $4.1 \times 10^5 \text{ M}^{-1}$  with the trend being HPD-1 > 29-22 > MOPC 315.

Purification of the three immunoglobulins by affinity chromatography showed that Dnp-glycine, used in the elution, could not be efficiently removed from either hybridoma, even after exhaustive dialysis. Dnp-glycine could, however, be easily removed from the active sites of MOPC 315. UV-visible spectroscopy and Scatchard analysis of the fluorescence data revealed only 52% and 50% of the active sites free for HPD-1, respectively, and only 42% and 43% of the active sites free for 29-22. The slight differences in measured affinities could not explain the drastic difference between the myeloma and the hybridomas.

Epr titrations of the hybridoma immunoglobulins with the paramagnetic probe Dnp-tmapo (Figure 2) revealed considerably less anisotropy associated with the spin probe when Dnp was bound in the active sites. Lateral dimensions for MOPC 315 with this spin label probe were determined by Dwek and coworkers to be 0.35 nm and 0.50 nm to either side of the spin label portion of the hapten [6]. Using a similar analysis of the epr spectra, the lateral dimensions for 29-22 were 0.50 nm, and >0.50 nm for HPD-1. Neither hybridoma distinguished between the enantiomers of the spin label. The rigidity of the spin label environment followed the trend MOPC 315 > 29-22 > HPD-1, just opposite the trend in affinities.

The immunoglobulin with the most rigid spin label environment had the lowest affinity toward Dnp-glycine and also released Dnp-glycine most readily. HPD-1 had the greater affinity while providing the more open environment for the spin label. In comparing the two hybridomas, the more open active site of HPD-1 released Dnp-glycine to a greater extent than 29-22. The narrowness of the active site pocket for MOPC 315 suggests that Dnp is structurally similar to a portion of a larger site-filling hapten so that the active site does not express any specificity to the immunogen backbone.





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# The Bis-Pocket Porphyrin: A Synthetic Analog for Heme Proteins

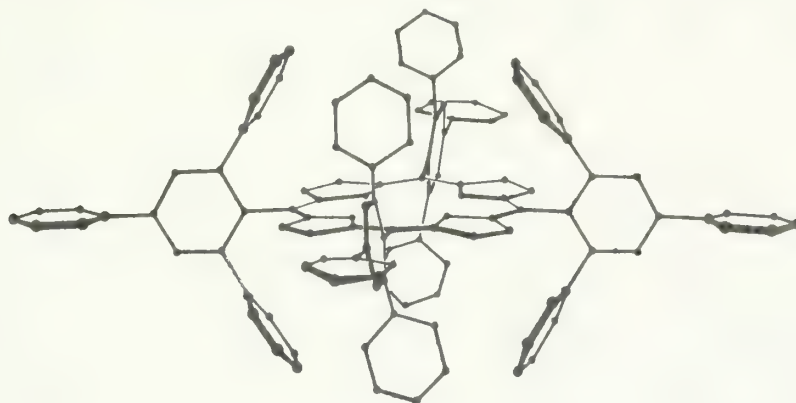
Mary M. Fox

Final Seminar

September 12, 1983

Porphyrin analog studies of heme containing proteins have had to overcome two major obstacles. These are the tendencies for iron porphyrins to oxidatively cleave at the meso-positions and to form the ferric  $\mu$ -oxo dimer under oxidative conditions [1,2]. Substituents introduced at the meso positions inhibit the porphyrin ring cleavage reaction. Furthermore, if the substituents at the meso-carbons are sufficiently bulky, the bimolecular reaction of two iron porphyrin species is prevented. Two of the more successful porphyrin model systems in dealing with the second obstacle have incorporated bulky substituents; these are Collman's [3] "picket-fence" and Baldwin's [4] "Capped" porphyrins.

A similar approach was used to develop a more versatile porphyrin system. The condensation of 2,4,6-triphenylbenzaldehyde with pyrrole in refluxing propionic acid produced 5,10,15,20-tetrakis-(2,4,6-triphenylphenyl)porphyrin or  $H_2TTPPP$ . The structural representation of  $H_2TTPPP$  is presented in the figure below.



CPK models of the porphyrin suggest a "pocket-like" nature to the steric protection hence the use of the more trivial name "Bis-Pocket" porphyrin. Insertion of iron into the "bis-pocket" porphyrin is accomplished using iron pentacarbonyl and iodine in refluxing toluene [5]. The ferric complex is reduced with  $(CH_3)_4NBH_4$  in THF. The 5-coordinate iron (II) complex is generated by the addition of a sterically hindered imidazole, 1,2-dimethylimidazole (1,2-Me<sub>2</sub>Im) [6].

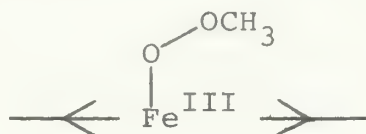
Fe(II)TTPPP(1,2-Me<sub>2</sub>Im) demonstrates reversible O<sub>2</sub> and CO binding [7] at room temperature. Reversible O<sub>2</sub> binding is observed at temperatures as high as 60°C with a corresponding half-life of 2.0 hours. Surprisingly, the oxygen affinity (expressed as the  $P_{1/2}$ ) of the "bis-pocket" porphyrin is 508 torr at 25° which is more than 10 times poorer than hemoglobin [8] and Collman's picket-fence complex [3]. This result cannot be accounted for in terms of steric encumbrance of the O<sub>2</sub> ligand by the "pockets" of TTPPP. Equilibrium



binding studies with the axial bases, N-methylimidazole and 1,2-Me Im, reveal the "pockets" do not impede the ligation of bulky axial ligands. Thermodynamic data likewise show no enthalpic barrier to coordination of  $O_2$  as compared with the "picket-fence" systems and hemoglobin and myoglobin. In contrast, Baldwin's "Capped" porphyrin shows an even lower  $O_2$  affinity ( $P_{1/2}=4000$  torr) under similar conditions. The explanation for the reduced affinity in the Capped system is believed to be due to distortion of the porphyrin macrocycle induced by the "cap" thus affecting the binding of all axial ligands [9].

A solvent dependent  $O_2$  affinity study shows that polarity of the solvent can modulate the  $O_2$  affinity by a factor of three. Using the solvents: mesitylene, toluene, benzene, chlorobenzene, dichlorobenzene (specifically chosen to minimize complicating effects due to solvent coordination or H-bonding), increased solvent polarity resulted in increased  $O_2$  affinity. Interestingly, the opposite effect is observed with CO affinities (i.e. increased solvent polarity diminishes CO affinity by a factor of two). The results of the  $O_2$  and CO binding studies with the "bis-pocket" porphyrin demonstrate that polarity can play an important role in modulating ligand affinities. It is believed that a similar polarity effect in the form of distal H-bonding [10] interactions may exist in biological systems as a means of discriminating  $O_2$  over CO. This is physiologically important as a mechanism for detoxifying against endogenously produced CO.

The versatility of the "bis-pocket" porphyrin as a model for a variety of biological heme systems is evidenced by its oxidative stability in the presence of a wide variety of oxidants: cumene and t-butyl hydroperoxides, peracetic and m-chloroperbenzoic acids, and iodosobenzene and iodoso-m-xylene. For comparison, chlorotetraphenylporphyrinatoiron (III) in the presence of methanol and iodoso-m-xylene decomposes in a matter of minutes, whereas the bis-pocket porphyrin under similar conditions, is stable for a period of days. Much of the current interest in porphyrin/oxidant systems is the hope of isolating and studying intermediates in the enzymic cycles of P-450 [11], catalase and peroxidase [12]. The reaction of Fe(III)-TTPPPCl with iodosobenzene (or any oxidant previously mentioned) and methanol generates an unusual red complex. NMR, EPR, UV-vis and titration results suggest the red species is:



The metalloalkylperoxide complex is not an active hydroxylating agent but can be reduced with sodium dithionite or phenyltrimethylammonium iodide to give quantitatively the original ferric species. Treatment of cyclohexene with Fe(III)TTPPPI in  $CH_2Cl_2$  without methanol present does give cyclohexene epoxide as its major oxidation product. Thus, the apparent role of methanol appears to be to stabilize the active oxygen atom transfer agent by trapping it as the metalloperoxide complex (i.e. the "red" species). Groves et al. [13]





have reported observing an  $\text{Fe}^{\text{IV}}=0$  species at low temperatures. Unusual highly oxidized iron species are believed to be the active intermediates of the catalytic cycle of P-450 and have been observed spectrally for the enzyme systems horseradish peroxidase [14] and peroxidases [15].

Of future interest is continued efforts in the oxidation chemistry of the bis-pocket porphyrin. The steric protection of the pockets allows one to mimic enzymatic substrate specificity and regio- and stereoselectivity [16], in for example shape selective alkane hydroxylation [17].

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## Electron Transfer in a Series of Mixed-Valence Copper(II)-Copper(I) Complexes

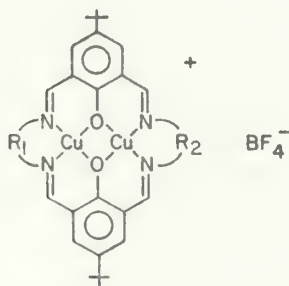
Russell C. Long

Final Seminar

September 13, 1983

The properties of mixed-valence complexes have been of interest to experimental and theoretical researchers for a considerable period of time [1-4]. Recently, it has been pointed out that the need is still present to expand the theoretical models in order to more thoroughly understand the experimental results [5]. Another approach is the one employed here, where physical measurements are used to more thoroughly examine the properties of a particular class of mixed-valence complexes. This approach involves finding a particular class of mixed-valence complexes that have dynamical behavior on the timescale of a particular spectroscopic technique and then to introduce perturbations in the ligation of these complexes that will alter their observed dynamical behavior.

Slight perturbations have been imposed on the Robson macrocyclic ligand [6]. Gagné, et al. [7] have shown that the mixed-valence copper(II)-copper(I) complex of this ligand exhibits dynamical behavior on the epr timescale. This complex exhibited epr delocalized behavior at room temperature and localized behavior at 175 K. The complexes used in this work [8] are similar to that used in Gagné's, except that t-butyl groups have replaced the methyl groups para to the phenolic oxygen and the diimine linkages were altered throughout the series of complexes, shown below:



- I.  $\text{R}_1=\text{R}_2=\text{PROPYLENE}$
- II.  $\text{R}_1=\text{R}_2=2,2'\text{-DIMETHYLPROPYLENE}$
- III.  $\text{R}_1=\text{R}_2=\text{BUTYLENE}$
- IV.  $\text{R}_1=\text{R}_2=2,2'\text{-BIPHENYLENE}$
- V.  $\text{R}_1=\text{PROPYLENE}$ ;  $\text{R}_2=2,2'\text{-DIMETHYLPROPYLENE}$
- VI.  $\text{R}_1=\text{PROPYLENE}$ ;  $\text{R}_2=2,2'\text{-BIPHENYLENE}$
- VII.  $\text{R}_1=\text{PROPYLENE}$ ;  $\text{R}_2=\text{BUTYLENE}$
- VIII.  $\text{R}_1=\text{R}_2=2\text{-HYDROXYPROPYLENE}$
- IX.  $\text{R}_1=\text{R}_2=1,3\text{ CYCLOHEXYLENE}$
- X.  $\text{R}_1=\text{PROPYLENE}$ ;  $\text{R}_2=1,8\text{ NAPHTHALENE}$
- XI.  $\text{R}_1=\text{PROPYLENE}$ ;  $\text{R}_2=2\text{-HYDROXYPROPYLENE}$





The binuclear copper(II) complexes were prepared via metal template synthetic routes and mixed-valence complexes were obtained by reducing the binuclear copper(II) complexes with sodium dithionite.

Complexes I, II, III, IV and IX were prepared to impose steric constraints upon the ligation system, without altering the electronic interaction between the metal centers. A transition from epr delocalized to epr localized behavior occurs for complexes I, II and III in solution. The transition temperature, that is, where the change from delocalized to localized behavior occurs, varied for these three complexes in increasing order; I, II and III. Invoking a coalescence model provided electron transfer rates at room temperature for these mixed-valence complexes, which increased in the same order. Complexes IV and IX possessed localized epr spectra at all temperatures. Results obtained from electrochemical, epr and electronic absorption measurements indicated that the copper(II) centers in complexes I, II and IX have an approximately square planar geometry, while the copper(II) sites in complexes III and IV are distorted somewhat from this geometry. Since copper(II) ions prefer a planar geometry, it is thought that the possession of non-planar geometric sites in these two complexes indicates considerable steric inflexibility, which will lead to slower rates of electron transfer. Complexes II and IX have slower rates of electron transfer when compared to complex I, which is probably caused by the greater bulkiness found in the ligands of II and IX. Spectroscopic properties indicate approximately constant electronic coupling in this series of complexes. The theoretical analyses of the intravalence electron transfer bands for these complexes do not correlate well with the electron transfer rates obtained from the epr measurements.

Complexes V, VI, VII and X were synthesized to obtain asymmetric mixed-valence complexes, where electron transfer should be slower. Complexes VI, VII and X were totally localized in solution at all temperatures on the epr timescale. Complex V exhibited the dynamical behavior of complex II and this was not very surprising since its symmetric analogs, I and II, were very similar in their physical properties. Frozen solution epr studies on complexes VI and VII indicated that the unpaired electron in these complexes is localized on the propylene site. The location of the unpaired electron is yet to be determined for complex X.

Complexes VIII and XI and complex XII, the complex identical to complex III except that its imine groups are reduced to amine groups, were prepared in order to alter the electronic interactions present in these complexes. Complexes VIII and XI were generally very similar in their physical properties when compared to complex I. The reduced ligand complex XII exhibited large differences in its physical properties over those observed for complex III. This complex has very slow rates of electron transfer as indicated by its epr spectra and IT band.

The magnetic exchange interactions for the binuclear copper(II) complexes indicate that the electronic coupling is relatively constant in these complexes. Typically, values between  $-380$  and  $-480 \text{ cm}^{-1}$  were recorded for the magnetic exchange coupling term,  $J$ , for these



complexes. The large values indicate a strong magnetic exchange interaction and thus strong electronic coupling. Complexes III, X and XII has reduced magnetic exchange coupling terms, in that order, in comparison to the other complexes.

Finally, the best description for determining when the transition from delocalized to localized behavior occurs using epr spectroscopy has not been decided upon as yet. Therefore, the epr spectra and the transition phenomenon in general need to be analyzed further.

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# Hetero- and Homobimetallic Complexes of New Hard-Soft Binucleating Ligands

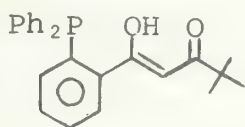
Debra A. Wroblewski

Final Seminar

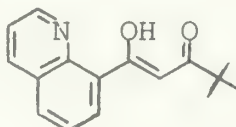
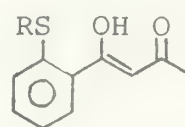
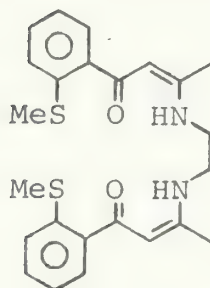
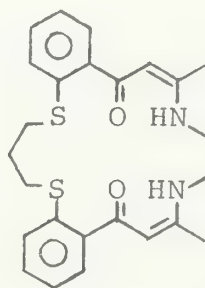
September 15, 1983

In recent years considerable inorganic research has been directed toward the preparation of binucleating ligands designed to hold two metals in close proximity. Reasons for continued interest in this area include the fact that complexes of this type are of potential importance in the development of new industrial catalysts [1] and in the simulation of biological catalytic systems [2]. Early researchers including Robson [3], Kida [4], Lintvedt and Glick [5], and Fenton [6] studied the coordination chemistry of ligands derived from the Schiff base condensation of either 3-formylsalicylic acid or 1,3,5-triketones with diamines. These ligands contain nitrogen and oxygen donor atoms which typically coordinate to "hard" 1st-row transition metals. More recently, researchers have prepared a number of bimetallic complexes using unsymmetrical "soft" ligands such as  $\text{Ph}_2\text{PC}_5\text{H}_4\text{N}$  [7] and  $\text{Ph}_2\text{PC}_5\text{H}_4^-$  [8,9,10]. Others have synthesized phosphine ligands incorporating crown ether-like [11,12] and Schiff-base [13] type sites which contain both "hard" and "soft" donor sites.

A unique feature of our unsymmetrical ligand systems is the arrangement of hard and soft donor atoms in a manner to preclude its functioning as a tridentate chelating agent. We have prepared a series of functionalized  $\beta$ -diketone ligand systems via the Claisen condensation of ortho-substituted methyl benzoate compounds with the potassium enolate of methyl ketones. The new binucleating ligands prepared in this work include phosphine, thioether and quinoline substituted  $\beta$ -diketones along with the Schiff-base derivatives of the thioether  $\beta$ -diketone, as shown below.



HacacP

Quinoline  
 $\beta$ -diketoneThioether  $\beta$ -diketone  
 $2\text{R} = 2\text{Me}, (\text{CH}_2)_3$  $\text{S}_2\text{O}_2\text{N}_2\text{H}_2$ cyclo- $\text{S}_2\text{O}_2\text{N}_2\text{H}_2$

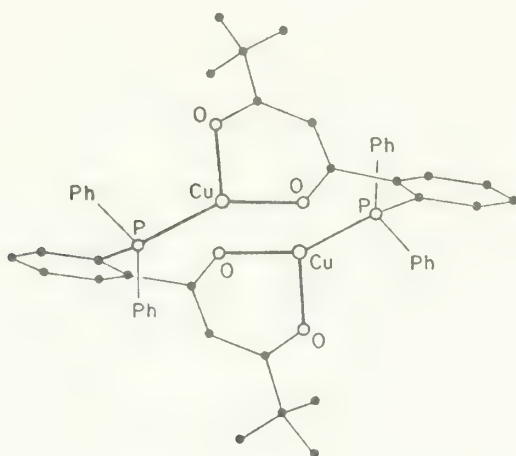




With these ligand systems we can exploit the extensive transition metal coordination chemistry of  $\beta$ -diketonates and of "soft" donor groups to prepare complexes containing two different metals.

Studies of monometallic complexes between  $\text{acacP}^-$  and  $\text{Ir(I)L}_2$  [ $\text{L}_2$  = cyclooctadiene or  $(\text{CO})_2$ ] [14] or  $\text{Ni(II)(C}_8\text{H}_{13})$  have demonstrated the dependence of the site selectivity of  $\text{acacP}^-$  on the  $\pi$  basicity of the metal ion.  $^{31}\text{P}$  NMR spectroscopy established that the  $\text{Ir(COD)}$  moiety occupies the P,O site while the  $\text{Ir(CO)}_2$  moiety occupies the O,O site. The  $\text{Ni(II)(C}_8\text{H}_{13})(\text{acacP})$  compound exhibits a third type of bonding; the ligand forms a P,C chelate in which the methine carbon bonds to nickel.

$\text{Cu}_2(\text{acacP})_2$  was prepared and its structure was shown to consist of two trigonally coordinated coppers situated in a face-to-face orientation [15]. This coordinatively unsaturated binuclear complex



undergoes  $1e^-$  oxidative addition with peroxy acids and peroxides [16] and readily reacts with molecular oxygen to give a stable crystalline derivative. Both of these processes give mixed valence compounds of the general type  $[\text{Cu}_2(\text{acacP})_2(\mu\text{-O}_2\text{CR})]$ .

Heterobimetallic complexes containing two  $\text{acacP}$  ligands [14] can be prepared systematically by two reaction sequences. One method involves insertion of the hard metal into the  $\text{O}_4$  compartment followed by coordination of a second, soft metal to the phosphine donors. Because of the incompatibility of phosphines with cupric salts, a second method must be employed for the preparation of  $\text{M-Cu(acacP)}_2$  complexes. This involves coordination of the phosphines to the soft metal followed by metalation of the  $\text{O}_4$  site. In this way the following heterobimetallic compounds were prepared:  $\text{ML}_2\{\text{M}'(\text{acacP})_2\}$ ,  $\text{M} = \text{Pt, Pd, Ru, Ir}$ ,  $\text{M}' = \text{Cu, Zn, TiCl}_2$ . An examination of this series by NMR, EPR and optical spectroscopy has been valuable in the assignment of structures as well as in determining the extent to which these two metals interact with one another.

Monometallic  $\text{Ni(II)}$  and  $\text{Cu(II)}$  derivatives of the new Schiff-base thioether ligand,  $\text{S}_2\text{O}_2\text{N}_2^{2-}$  and cyclo- $\text{S}_2\text{O}_2\text{N}_2^{2-}$  have been prepared along with a new binuclear copper complex.



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The Chemistry of Bis(cyclopentadienyl)divanadium Tetrasulfide:  
Elucidation of Ligand Dependent Reactivity and the Influence of  $\pi$ -Bonding

C. Mark Bolinger

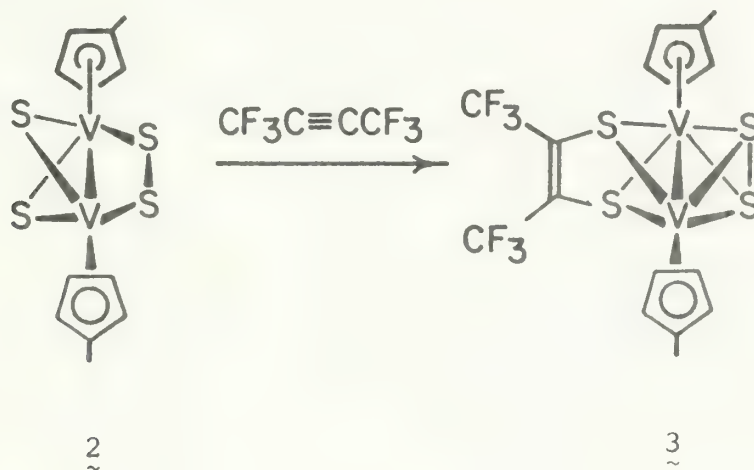
Final Seminar

October 13, 1983

There is now reason to suggest that binding and activation of unsaturated organic [1] and inorganic substrates [2,3] by metal sulfides occurs at the sulfur ligands and not at the metal. These exciting developments considerably broaden the scope and chemical significance of the nonmetal component in transition metal-nonmetal hybrids.

The concept of ligand to metal donation of electron density [4] via  $\pi$ -type orbitals is especially important for understanding the chemistry of the cyclopentadienyl vanadium sulfides since it is the sulfur ligands which interact with external reagents. Furthermore, systematic investigations of  $\pi$  bonding in multinuclear complexes are relatively rare [5] and are important for understanding the chemistry of both discrete and nonmolecular metal sulfides.

The synthetic entry into cyclopentadienylvanadium sulfide chemistry is provided by  $(RC_5H_4)_2V_2S_5$  (1), which was first reported in 1966 [6]. The disposition of the sulfur ligands in this compound was unknown until the preparation and structural characterization of  $(CH_3C_5H_4)_2V_2S_5$ , which revealed the presence of a transverse disulfide ( $\mu-\eta^2-S_2$ ), a parallel disulfide ( $\mu-\eta^1-S_2$ ), and a bridging sulfide ( $\mu-S$ ) [7]. Desulfurization of the  $30e^-$  complex 1 by tri-*n*-butyl phosphine ( $PBu_3$ ) produces the  $26e^-$  complex  $(RC_5H_4)_2V_2S_4$  (2).

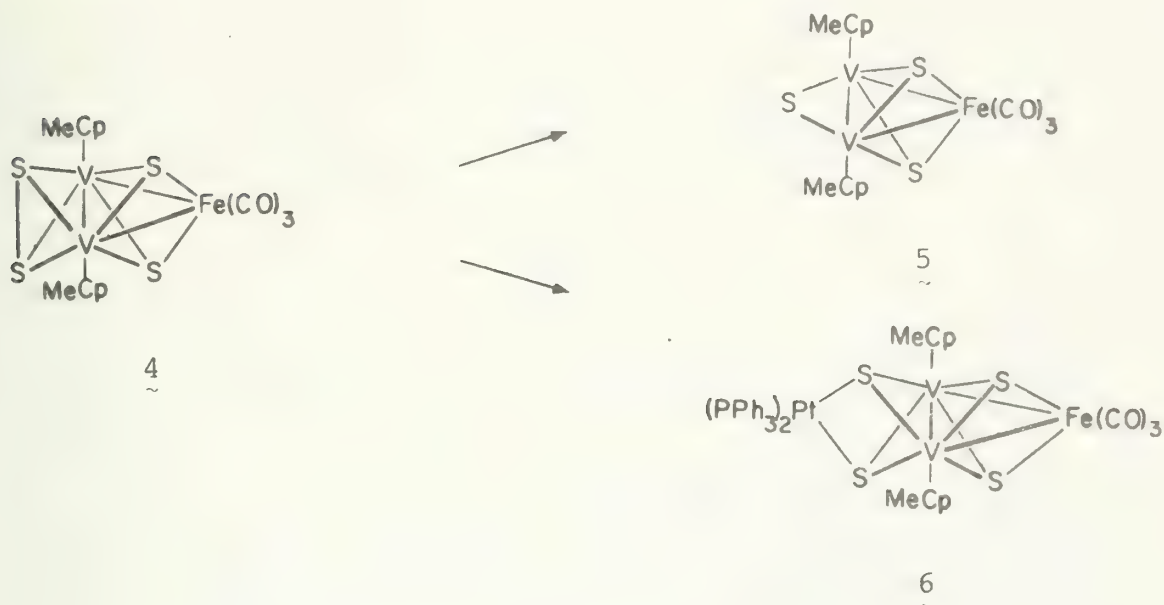


An analysis of the V-S distances in the electron deficient 2 provides evidence for efficient  $\pi$  donation from the bridging sulfides. Reaction of 2 with the electrophilic acetylene hexafluoro-2-butyne results in the formation of a dithiolene complex,  $(C_5H_5)_2V_2S_2(S_2C_2(CF_3)_2)$  (3) via attack at the nucleophilic  $\mu-S$  ligands. During this process, the  $\mu-\eta^1-S_2$  rotates to a  $\mu-\eta^2$  geometry, apparently as a result of decreased  $\pi$  donation from the bridging sulfides.



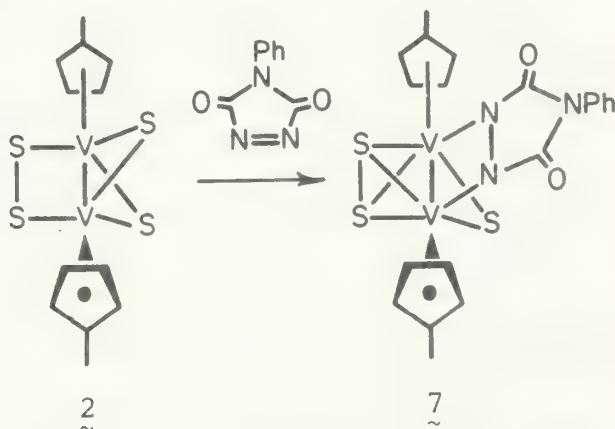


Treatment of **2** with  $\text{Fe}(\text{CO})_5$  in the presence of  $(\text{CH}_3)_3\text{NO}$  results in the formation of  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_4\text{Fe}(\text{CO})_3$  (**4**), the first example of a vanadium-iron cluster. Like the product of the acetylene reaction,



**4** contains a  $\mu\text{-}\eta^2\text{-S}_2$  ligand. This  $\mu\text{-}\eta^1\text{-S}_2$  ligand is electrophilic, reacting with  $\text{PBU}_3$  to produce  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_4\text{Fe}(\text{CO})_3$  (**5**) and with  $\text{Pt}(\text{PPh}_3)_2\text{C}_2\text{H}_4$  to produce  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_4\text{Fe}(\text{CO})_3\text{Pt}(\text{PPh}_3)_2$  (**6**) [8]. The solid state structures of **4** ( $48e^-$ ) and **5** ( $44e^-$ ) suggest that both V-Fe and V-S  $\pi$ -interactions are important for understanding the electronic structure of these clusters.

Compound **2** reacts with 4-phenyl-1,2,4-triazoline-3,5-dione (PTD) [9] to yield  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_3$  (PTD) (**7**). Structural characterization



of the  $\text{Pt}(\text{PPh}_3)_2$  derivative indicates that **7** possesses  $\mu\text{-S}$ ,  $\mu\text{-}\eta^2\text{-S}_2$ , and  $\mu\text{-}\eta^1\text{-PTD}$  ligands. Desulfurization of **7** produces  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_2$  (PTD) (**8**) which is structurally analogous to **2**. Further reaction



of 8 with PTD forms  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{V}_2\text{S}_2(\text{PTD})_2$  (9). The  $\mu\text{-}\eta^2\text{-S}_2$  ligand of 9 apparently results from oxidative coupling of two  $\mu\text{-S}$  ligands and is the first direct observation of this type of reaction.

Compound 2 can be further desulfurized by  $\text{PBU}_3$  to form higher nuclearity vanadium clusters,  $(\text{RC}_5\text{H}_4)_4\text{V}_4\text{S}_4$  (10) (a cubane [10]) and  $(\text{RC}_5\text{H}_4)_5\text{V}_5\text{S}_6$  (11) (structurally analogous to the known  $(\text{C}_5\text{H}_5)_5\text{V}_5\text{O}_6$  [11]), with interesting structural and magnetic properties. The  $56e^-$  complex 10 is the most electron deficient organotransition metal cubane to date. Theoretical studies on  $(\text{C}_5\text{H}_5)_4\text{M}_4\text{A}_4$  compounds predict that a  $56e^-$  cluster should be diamagnetic with  $\text{D}_{2d}$  symmetry [12]. However, compound 10 is paramagnetic with nearly ideal  $\text{T}_d$  symmetry.

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# High Pressure Nuclear Magnetic Resonance Studies in Inorganic Chemistry

David G. Vander Velde      Literature Seminar

October 18, 1983

The principal application of high pressure nuclear magnetic resonance in inorganic chemistry to date has been studies of solvent exchange on metal ions [1]. These studies have advanced mechanistic understanding of this fundamental process; exchange on most ions was too fast to study with earlier high pressure studies by spectrophotometry or isotopic dilution [2]. The parameter being sought in these studies is the volume of activation,  $\Delta V^\ddagger$ , which in the expected absence of electrostrictive effects is directly diagnostic of an associative (A or  $I_a$ ) or dissociative (D or  $I_d$ ) mode of activation for the exchange. The volume of activation determined by high pressure NMR is frequently simpler to interpret and less subject to systematic error than the entropy of activation determined by variable temperature NMR.

Various hardware configurations have been used for high pressure NMR, but the one most frequently used is a nonspinning sample inside a nonmagnetic pressure vessel, the pressure being applied by a fluid [3,4]. The exchange rates are derived from lineshape analysis by the Swift-Connick equations with correction for possible paramagnetic relaxation contributions to the second and subsequent solvation shells [5].

Mechanistic results obtained with high pressure NMR studies of solvent exchange include the surprising finding of a mechanistic crossover at iron among the divalent first row transition metal ions. This has been confirmed for water exchange [6] and nonaqueous solvent exchange [7], with good agreement between studies conducted using different nuclei [8]. Studies of the trivalent ions show a similar crossover; water exchange from iron (III) was shown to proceed by two mechanisms--I for  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  and  $I_d$  for  $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$  [9]. Variations in activation parameters including  $\Delta V^\ddagger$  were interpreted to indicate a change in the mechanism of dimethylformamide exchange from  $I_d$  to D occurring at Er [3].

A significant area of future application for high pressure NMR may be in studies of homogeneous catalysis. A study of the  $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$  cluster (one cluster present in a catalytic system for synthesis of ethylene glycol) showed that it gave  $[\text{Rh}_5(\text{CO})_{15}]$  quantitatively when pressurized under CO and  $\text{H}_2$ ; no further fragmentation was observed at pressures up to 1 kbar. Also, the exchange of free and bound CO was slow on the NMR timescale [10]. Observation of intermediates formed under reaction conditions may thus be possible for many homogeneous catalysts.





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# Reactions of Dichalcogenide and Substituted Dichalcogenide Ligands of Molecular and Nonmolecular Compounds

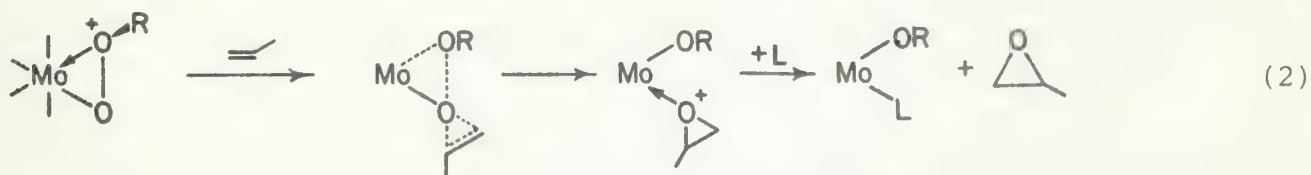
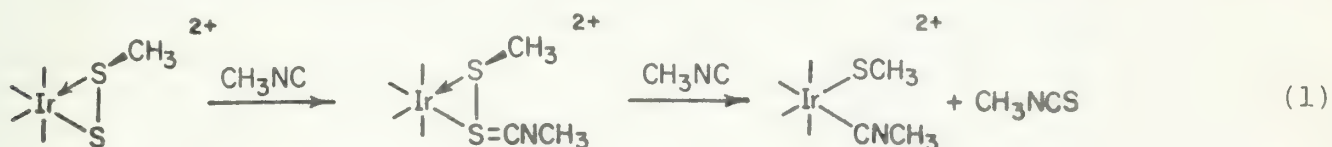
John E. Hoots

Final Seminar

October 20, 1983

Recently interest in side-bonding or  $\eta^2$ -ligands which contain chalcogens (O, S, Se) is accelerating with a wide variety of organic and inorganic systems being studied [1-3]. Three recent examples of significant work with the  $\eta^2$ -ligands have involved formation of an  $\eta^2$ -acetyl ligand by reversible CO insertion into a Zr-CH<sub>3</sub> bond [4], step-wise reduction of a thiocarbonyl ligand to CH<sub>3</sub>SH via an  $\eta^2$ -thioformyl intermediate [5], and X $\alpha$ -calculations probing the nature of bonding in  $\eta^2$ -E<sub>2</sub> complexes (E = O, S, Se) [6].

The formation of octahedral [Ir( $\eta^2$ -E<sub>2</sub>)(dppe)<sub>2</sub>]<sup>+</sup> (E = S, Se and dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) complexes is generally accomplished by "oxidative-addition" of pure chalcogens (S<sub>8</sub> or Se<sub>8</sub>) to [Ir(dppe)<sub>2</sub>]<sup>+</sup> [7]. Chalcogen transfer from (MeCp)<sub>2</sub>TiE<sub>5</sub> (E = S, Se) permitted similar conversions with a unique metallocycle, 1,4-[(MeCp)<sub>2</sub>Ti]<sub>2</sub>S<sub>4</sub>, co-produced with the Ir-S<sub>2</sub> complex. In the formation of the Ir-Se<sub>2</sub> compound, a significant rate enhancement (x 1000) was noted, as compared to the Se<sub>8</sub> method. The Ir-S<sub>2</sub> and -Se<sub>2</sub> complexes reacted with potent electrophiles such as CH<sub>3</sub>SO<sub>3</sub>F and CF<sub>3</sub>SO<sub>3</sub>H to form [Ir( $\eta^2$ -E<sub>2</sub>R)(dppe)<sub>2</sub>]<sup>2+</sup> (R = CH<sub>3</sub>, H and E = S, Se) [8]. The pyramidal nature of the alkylated chalcogen atom was demonstrated by the observation of resonances for diastereomeric complexes in the 360 MHz <sup>1</sup>H NMR spectra. The  $\eta^2$ -S<sub>2</sub>CH<sub>3</sub> complex is very reactive toward nucleophiles (CH<sub>3</sub>NC, CN<sup>-</sup>, and PPh<sub>3</sub>) and a variety of reaction pathways have been elucidated. In particular, the reaction involving CH<sub>3</sub>NC was shown to involve at least two steps (eq. 1) and serves as a model for the Oxirane olefin epoxidation process (eq. 2) [9].

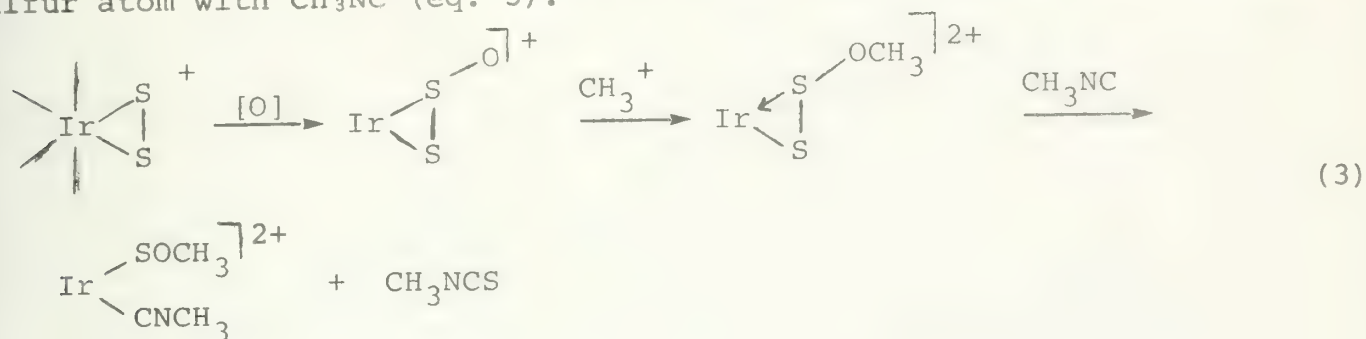


The use of organoperacids permitted rapid, clean oxidations of the Ir-S<sub>2</sub> and Se<sub>2</sub> complexes to the corresponding  $\eta^2$ -S<sub>2</sub>O, S<sub>2</sub>O<sub>2</sub>, and Se<sub>2</sub>O compounds. Similarly, oxidation of Cp<sub>2</sub>Nb( $\eta^2$ -S<sub>2</sub>)Cl produced an  $\eta^2$ -S<sub>2</sub>O unit. Peracids were also used to effect the facile conversion of  $\mu_3$ -S to  $\mu_3$ -SO ligands in the syntheses of Fe<sub>3</sub>(CO)(S)(CO)<sub>9</sub> and Fe<sub>2</sub>Pt(SO)(S)(CO)<sub>6</sub>(PPh<sub>3</sub>)<sub>2</sub>, which represent the only sulfur-monoxide complexes presently known [10]. Only the triiron complex has been previously reported and was a by-product from the synthesis of Fe<sub>3</sub>(S)<sub>2</sub>(CO)<sub>9</sub> [11]. Reactivity studies on the E<sub>2</sub>O, S<sub>2</sub>O<sub>2</sub> and SO ligands indicated transfer of the exocyclic oxygen atom to be very



difficult in sulfur-based systems but relatively facile for the  $\eta^2\text{-Se}_2\text{O}$  ligand.

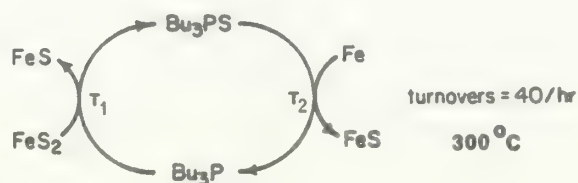
Attempted syntheses of complexes containing the elusive  $\eta^2\text{-EO}$  ( $\text{E}=\text{S}, \text{Se}$ ) ligands by abstraction of the unsubstituted chalcogen in the  $\eta^2\text{-E}_2\text{O}$  groups were not successful. However, the analogous and previously unknown  $\eta^2\text{-SeS}$  ligand was synthesized with  $[\text{Ir}(\text{dppe})_2]^+$  and the chalcogen-transfer reagent,  $\text{Cp}_2\text{TiS}_x\text{Se}_{5-x}$  ( $x \approx 2$ ). A stabilized form of the SO unit, the O-methyl thioperoxide ligand, was observed in  $[\text{Ir}(\eta^1\text{-SOCH}_3)(\text{CH}_3\text{NC})(\text{dppe})_2]^{2+}$  and was synthesized from the  $\eta^2\text{-S}_2\text{O}$  complex by O-alkylation, followed by abstraction of the unsubstituted sulfur atom with  $\text{CH}_3\text{NC}$  (eq. 3).



The appearance of high-field shifted ortho-phenyl resonance(s) for all cis- $[\text{Ir}(\text{X})(\text{Y})(\text{dppe})_2]^{n+}$  complexes [12] is particularly distinctive. A new theory based on mutual shielding effects of the aromatic rings is proposed from solution and solid-state structural studies of the cis-iridium complexes.

The research on monomeric  $\eta^2\text{-dichalcogenide}$  complexes has been extended to desulfurization of solid-state, extended-lattice metal sulfides, particularly pyrite ( $\text{FeS}_2$ ). The formation of pollutants, such  $\text{SO}_2$ , from the decomposition of pyrite has remained a major barrier to increased use of coal as a fuel source. We found that pyrite is desulfurized at  $\sim 260^\circ\text{C}$  with  $(n\text{-C}_4\text{H}_9)_3\text{P}$  to an equilibrium mixture of  $\text{FeS}$  and  $\text{Fe}_{0.95}\text{S}$  (pyrrhotite), as determined by x-ray powder diffraction and Mössbauer spectroscopy [13,14]. The phosphine desulfurization reaction was successfully applied to a sample of Illinois coal (1.9%  $\text{FeS}_2$ ) with x-ray powder diffraction revealing complete conversion of pyrite to pyrrhotite. Also, partial desulfurization of a spectrum of metal sulfides ( $\text{MoS}_3$ ,  $\text{CoS}_2$ , and  $\text{Cu}_2\text{S}$ ) was successful. Addition of a sulfur-receptor, such as metallic iron, created a catalytic cycle (shown below) with 40 turnovers/hour observed for an 100:1 ratio of  $\text{FeS}_2$  to  $(n\text{-C}_4\text{H}_9)_3\text{P}$  at  $\sim 300^\circ\text{C}$ . The desulfurization of  $\text{FeS}_2$  with  $\text{Fe}$  under a CO atmosphere at  $400^\circ\text{C}$  indicated other catalytic cycles, such as the CO-COS couple [15,16], may exist and be potentially useful in future coal desulfurization processes.

#### Desulfurization Cycle







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November 4, 1983

We have found that the treatment of  $M_3(CO)_{12}$  ( $M = Ru, Os$ ) with sodium in ether solvents at various reaction temperatures provides selective formations of several large anionic carbonyl clusters of ruthenium and osmium [2]. This synthetic approach is analogous to the thermal condensation of a 5:1 mole ratio of  $Fe(CO)_5$  and  $Fe(CO)_4^{2-}$ , which is obtained from the reduction of  $Fe(CO)_5$  by sodium [3], to generate  $Fe_6C(CO)_{16}^{2-}$  [4]. Thus, the reaction of  $Ru_3(CO)_{12}$  and one equivalent of sodium ( $Ru_3:Na = 1:1$ ) affords  $Ru_6(CO)_{18}^{2-}$  (1) [5] in refluxing tetrahydrofuran ( $66^\circ C$ ), but  $Ru_6C(CO)_{16}^{2-}$  (2) [6] in refluxing diglyme ( $162^\circ C$ ). Under the



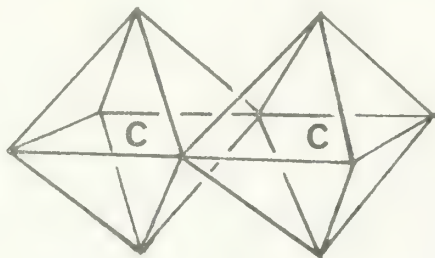
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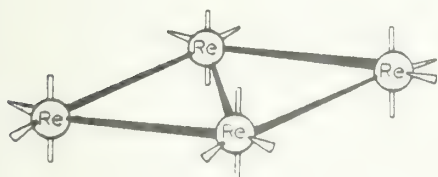
formulated as  $\text{Os}_6\text{C}(\text{CO})_{17}$  is isolated in low yield from the oxidation of reaction mixtures produced upon prolonged pyrolysis of  $\text{Os}_6(\text{CO})_{18}^{2-}$  ( $162^\circ\text{C}$ ). This is suggested as evidence for the formation of  $\text{Os}_6\text{C}(\text{CO})_{16}^{2-}$  under the conditions for conversion of  $\text{Os}_6(\text{CO})_{18}^{2-}$  to  $\text{Os}_{10}\text{C}(\text{CO})_{24}^{2-}$ .

Extended pyrolysis of  $\text{Ru}_6\text{C}(\text{CO})_{16}^{2-}$  also provides a decanuclear cluster, but  $\text{Ru}_{10}\text{C}_2(\text{CO})_{24}^{2-}$  (5) has two carbide ligands. The structural analysis of  $\text{Ru}_{10}\text{C}_2(\text{CO})_{24}^{2-}$  [9] shows the carbido-metallic framework to have approximate  $D_2$  symmetry and is based on two essentially octahedral moieties fused at a common equatorial edge. The limiting low temperature  $^{13}\text{C}$  NMR spectrum of 5 shows a pattern fully consistent with the solid state structure.

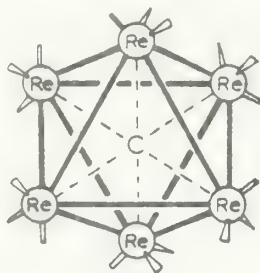


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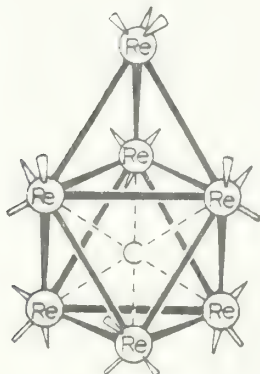
Treatment of  $\text{Re}_2(\text{CO})_{10}$  with sodium ( $\text{Re}_2:\text{Na} = 1:1$ ) in diglyme at  $150^\circ\text{C}$  affords  $\text{Re}_4(\text{CO})_{16}^{2-}$  (6) [10], which in refluxing diglyme is converted predominantly to  $\text{H}_2\text{Re}_6\text{C}(\text{CO})_{18}^{2-}$  (7) [11]. In the latter transformation  $\text{Re}_7\text{C}(\text{CO})_{21}^{3-}$  (8) [12] and  $\text{Re}_8\text{C}(\text{CO})_{24}^{2-}$  (9) [13] are obtained as minor products. These clusters have



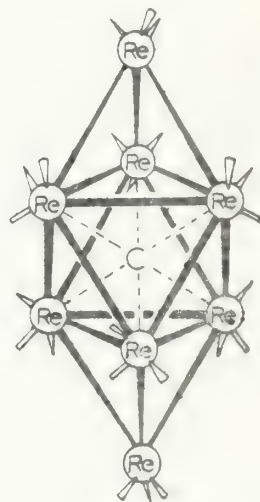
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9





been prepared selectively by employing the appropriate stoichiometric ratio of  $\text{Re}_2(\text{CO})_{10}$  and sodium ( $\text{Re}_2:\text{Na} = 3.5:3$  for 8 and  $4:2$  for 9) in triglyme ( $190-210^\circ\text{C}$ ). In both syntheses  $\text{Re}_4(\text{CO})_{16}^{2-}$  and then  $\text{H}_2\text{Re}_6\text{C}(\text{CO})_{18}^{2-}$  are the intermediates observed prior to the formation of 8 or 9. The evolution of carbon dioxide also is observed in the conversion of  $\text{Re}_4(\text{CO})_{16}^{2-}$  to the three carbide clusters (7, 8, and 9).

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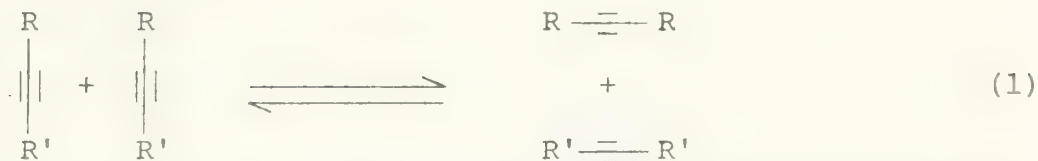


# ALKYNE METATHESIS REACTIONS

Wen-Yann Yeh

Literature Seminar

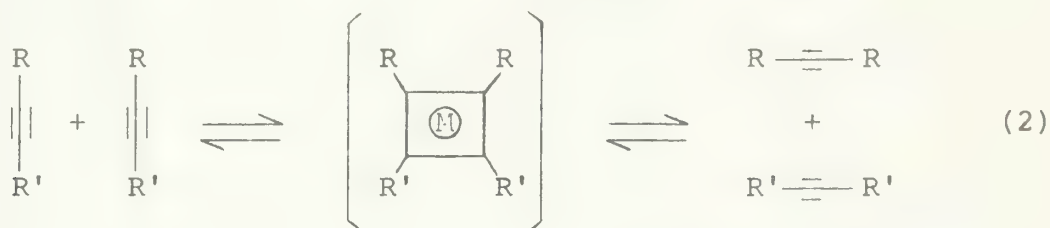
November 10, 1983



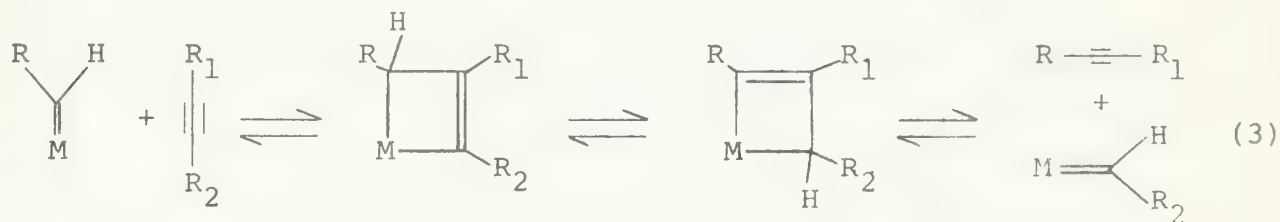
The first alkyne metathesis reactions (Fig. 1) were reported by Pennella [1] in 1968. Since then a limited number of heterogeneous and homogeneous catalytic systems have been found. The heterogeneous catalytic systems, such as  $\text{MoO}_3/\text{SiO}_2$  and  $\text{WO}_3/\text{SiO}_2$  [1-5], also function as olefin metathesis catalysts, but the conditions for these reactions are normally harsher than the related olefin reactions. In homogeneous catalytic systems, Mortreux [6-8] has observed that  $\text{Mo}(\text{CO})_x\text{Ly-PhOH}$  combinations and  $\text{O}_2\text{Mo}(\text{acac})_2\text{-AlEt}_3\text{-PhOH}$  combinations catalyze alkyne metathesis while Schrock [9-11] has observed similar reactions with tungsten alkylidyne complexes.

The homogeneous systems have been investigated more thoroughly than the heterogeneous systems. A number of mechanisms for this reaction have been suggested. These include the following (Eq. 2-5):

## A. Cyclobutadiene Complex Intermediates [1]

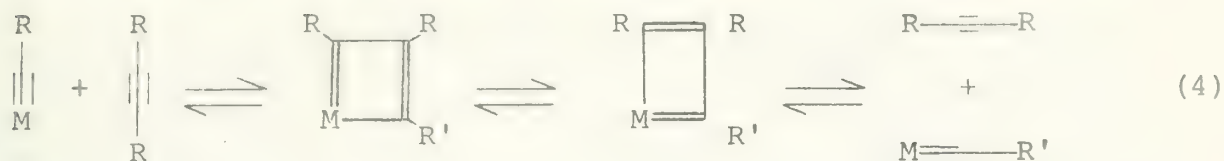


## B. Metal-carbene and Metallacyclobutene Intermediates [8]



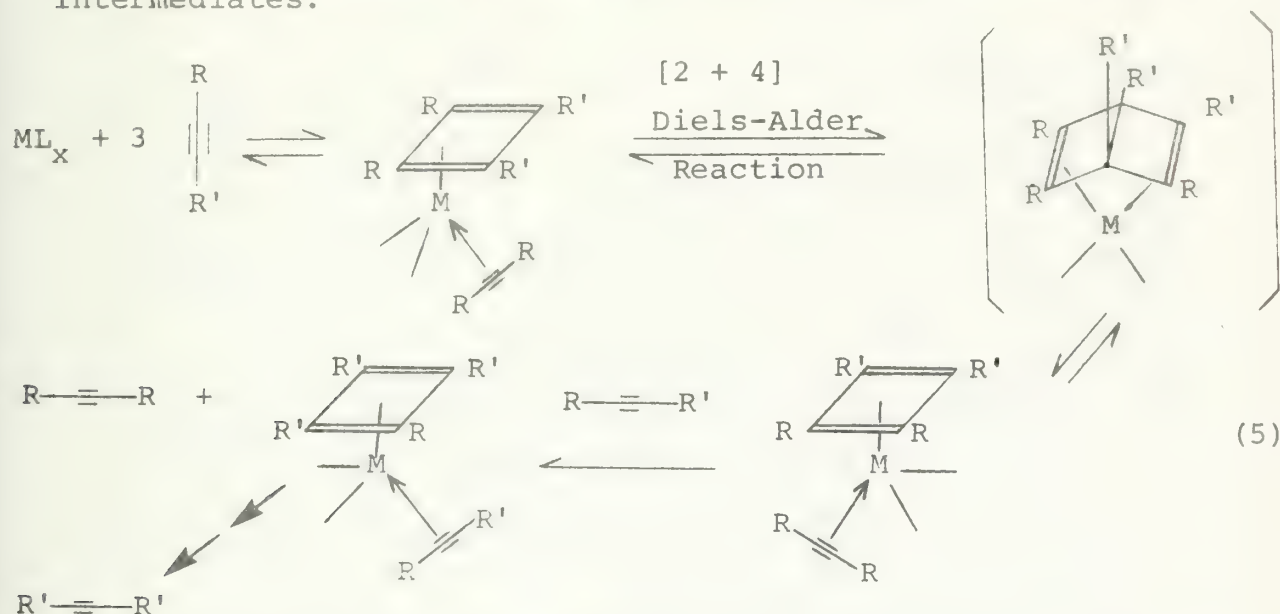


### C. Metal-carbyne and Metallacyclobutadiene Intermediates [12]



The preparation and reactivities of cyclobutadiene-metal complexes reported by Hubel [13] and Criegee [14-16] suggest that another mechanism for alkyne metathesis might also be possible:

### D. Diels-Alder Reactions on the Acetylene Cyclobutadiene Complex Intermediates.



Some catalysts (eg.  $(\text{Bu}^t\text{O})_3\text{W}(\text{CBu}^t)$  and  $\text{O}_2\text{W}(\text{acac})_2\text{-AlEt}_3\text{-PhOH}$ ) show outstanding activity (300 turnovers/min) and selectivity (97% alkyne products) suggesting that alkyne metathesis may become a viable process in industry. However, the exact mechanism is still open to much speculation. It appears that the mechanism may be dependent on the specific reaction system, such as the specific catalyst and alkynes being utilized. The details remain a considerable challenge to organometallic chemists.

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## Applications of Nuclear Quadrupole Double Resonance Spectroscopy

Peter M. Woyciesjes

Final Seminar

November 29, 1983

Since its discovery in 1951, Nuclear Quadrupole Resonance (NQR) spectroscopy has been used to study the electronic environment around quadrupolar nuclei. However, the low sensitivity of direct methods for detecting the transitions of lighter quadrupolar nuclei ( $^2\text{H}$ ,  $^{10,11}\text{B}$ ,  $^{17}\text{O}$ ,  $^{25}\text{Mg}$ , etc.) has severely limited the usefulness of NQR spectroscopy. Drastic improvements in the sensitivity and spectroscopic range of the NQR technique were made with the advent of double resonance NQR techniques [1]. Quadrupolar nuclei previously inaccessible to traditional methods are now detectable at concentrations of  $10^{-6}$  of the abundant nuclear spin, making NQR spectroscopy an important tool for the study of the solid state electronic structure of molecules.

NQR spectroscopy measures the interaction of a nucleus, possessing an electronic quadrupole moment  $Q$ , with the electric field gradient produced at the nucleus by its local electronic environment. As a result, the NQR technique provides information on the ground state charge distribution in the vicinity of the quadrupolar nucleus.

In this work the  $^{14}\text{N}$  and  $^{17}\text{O}$  NQR spectra for a series of substituted aromatic amine oxides was utilized to probe the electronic nature of the N-O group. Aromatic amine oxides have elicited considerable chemical [2], pharmacological [3], and theoretical interest [4]. Fundamental to their chemistry is the dual pi electron, donor-acceptor role of the NO moiety. With the aid of  $^{13}\text{C}$  CP-MAS NMR [5,6] the orientation of electric field gradient (efg) tensor of the N-O group has been determined. Using a modified Townes-Dailey model [7], analyses of the hydrogen bonding, coordination, and ring substitution effects on the nature of the N-O group are interpreted in terms of the nitrogen valence p orbital population. Further, the Z axis of the  $^{17}\text{O}$  efg tensor has been shown to lie along the N-O bond. Analysis of the  $^{17}\text{O}$  NQR results of the oxide group oxygen for a series of substituted pyridine-N-oxides proves a quantitative measure of the sensitivity of the pi-bond order to variations in the para substituent. Changes in the solid state N-O pi-bond order correlate with shifts in the N-O stretching frequency [8], as well as with  $^{17}\text{O}$  and  $^{15}\text{N}$  NMR chemical shifts in solution [9,10].

The  $^2\text{H}$  and  $^{14}\text{N}$  NQR spectra for a series of urea adducts were studied to develop a better understanding of the nature and extent of charge transfer that occurs in the peptide linkage,  $-\text{CONH}_2$ , upon the formation of N-H---O and O-H---O hydrogen bonds. Urea, a basic biological building block, was chosen for study because of its ability to form a large variety of adducts which exhibit varying degrees of hydrogen bonding. The NQR results along with crystallographic data [11] show the existence of a correlation between H---O contact distance and the C-O bond length. There is lengthening of the C-O bond with decreasing O---H contact distance. In terms



of classical valence bond theory, other canonical forms become increasingly important with increasing protonation of the carbonyl oxygen. Crystallographic data indicate the presence of an inverse relationship between C-O and C-N bond lengths, through a range of 1.30-1.40Å and 1.30-1.20Å respectively. A variation of ~0.1Å (about 0.5 bond order) indicates a dramatic variation in the electronic structure of the amide framework. The  $^2\text{H}$  and  $^{14}\text{N}$  NQR data provide quantitative measures of electronic changes as well as the variations in valence shell orbital populations that occur with changing hydrogen bond order.

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# The Synthesis of $\text{Re}_2\text{Pt}(\text{CO})_{12}$ and its Use as a Catalyst Precursor

Michael A. Urbancic

Final Seminar

December 1, 1983

In the past few years the use of transition metal carbonyl compounds as precursors to oxide- and polymer-supported catalysts has expanded tremendously [1]. The use of mixed-metal compounds for the preparation of bimetallic catalysts is of particular interest, since such compounds may allow the formation of catalytically active sites of well-defined composition. Several reviews on mixed-metal compounds have appeared recently [2].

One of the most important commercial bimetallic catalysts is alumina-supported platinum-rhenium, which is used in the catalytic reforming of petroleum naphthas [3]. To date, however, only a few molecular bimetallic compounds of platinum and rhenium have been reported [4], and all of them contain phosphine ligands. This is an undesirable feature for a catalyst precursor, in that supported metal particles generated from such compounds may be poisoned by phosphorous. The preparation of platinum-rhenium bimetallic compounds that contain easily removable ligands is therefore a desirable goal.

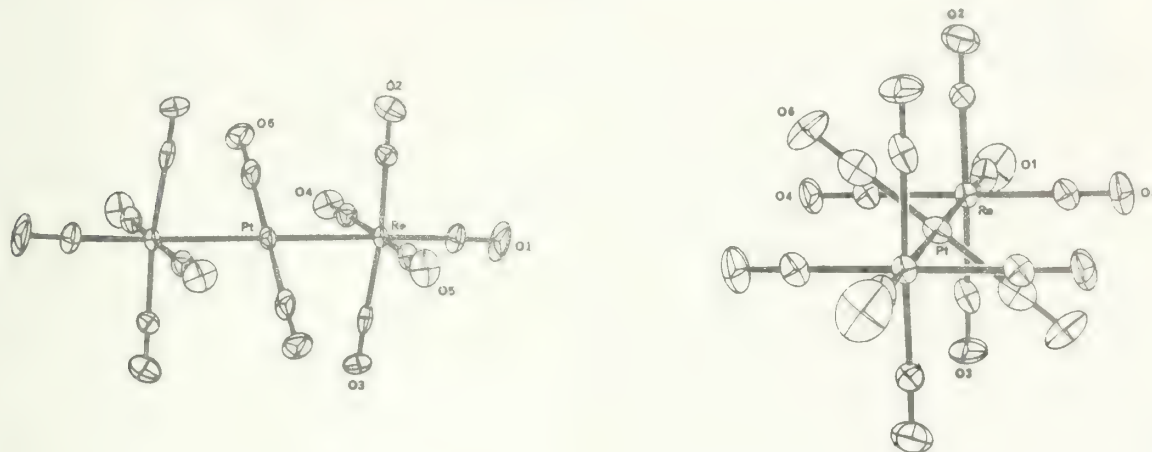
Recently, the reaction of metal hydrides with metal alkyl compounds has been used to prepare mixed-metal species via "binuclear reductive elimination" [5]. This approach has been used to prepare the heterobimetallic compounds  $\text{Re}_2\text{Pt}(\text{CO})_{12}$  and  $\text{Mn}_2\text{Pt}(\text{CO})_{12}$  by the reaction of  $\text{HM}(\text{CO})_5$  ( $\text{M} = \text{Re}, \text{Mn}$ ) [6] with  $\text{Me}_2\text{Pt}(\text{COD})$  ( $\text{COD} = 1,5\text{-cyclooctadiene}$ ) [7]. A single-crystal X-ray diffraction analysis of  $\text{Re}_2\text{Pt}(\text{CO})_{12}$  shows that the molecule ideally possesses  $\text{D}_{2h}$  symmetry with octahedral coordination about each rhenium atom and square planar (trans) geometry about the platinum atom (see Figure).

The  $\text{Re}_2\text{Pt}(\text{CO})_{12}$  cluster has been supported on activated alumina and decomposed by temperature programmed heating in flowing  $\text{H}_2$ . Although some fragmentation of the cluster occurs during impregnation, the decomposition profile shows that methane formation occurs at a significantly lower temperature than for a rhenium-only catalyst prepared from  $\text{Re}_2(\text{CO})_{10}$ .

The reduced catalysts derived from  $\text{Re}_2\text{Pt}(\text{CO})_{12}$  have been characterized by selective chemisorption measurements, temperature programmed decomposition of adsorbed CO, as well as by the following catalytic reactions: CO methanation, propylene metathesis, and ethane or n-butane hydrogenolysis. Catalysts prepared from conventional precursors [ $(\text{NH}_3)_2\text{Pt}(\text{NO}_2)_2 + \text{NH}_4\text{ReO}_4$ ] show significant differences in catalytic behavior. For example, the cluster-derived catalysts exhibit higher activities (2-3x at 225°C) and higher apparent activation energies (~6 kcal/mole) for the hydrogenolysis reactions. This is of particular interest in view of the fact that Pt-Re/ $\text{Al}_2\text{O}_3$  catalysts prepared under conditions



expected to enhance bimetallic particle formation exhibited pronounced hydrogenolysis activity [8]. Enhanced activity has also been observed for Pt-Re/SiO<sub>2</sub> and bulk Pt-Re alloys [9]. Treatment of the reduced cluster-derived catalyst in air at elevated temperature followed by a second H<sub>2</sub> reduction, changes the catalyst in such a way that its catalytic properties are nearly identical to those of a conventionally-prepared catalyst. Taken altogether, these observations are consistent with the presence of bimetallic particles in the cluster-derived catalysts, while under oxidizing conditions, segregation of the individual metals presumably occurs.



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## Inorganic Chemistry in Room Temperature Molten Salts

Clarke W. Earley

Literature Seminar

December 8, 1983

The first room temperature molten salt was reported by Hurley and Wier in 1951 [1]. Mixing  $\text{AlCl}_3$  and ethylpyridinium bromide in a 2:1 mole ratio causes a spontaneous and exothermic reaction. The resulting liquid is a light gold color if the starting materials are carefully purified. Upon electrolysis for two to three weeks, the solution becomes colorless [2]. The resulting liquid is hygroscopic and is oxidized by air. It was found that this liquid is miscible with benzene in all proportions up to a 50% volume ratio. In 1979, Robinson and Osteryoung reported a new system based on  $\text{AlCl}_3$  and n-butylpyridinium chloride (BPC) [3]. Since that time, several new ambient temperature molten salts based on  $\text{AlCl}_3$  and various organic salts have been reported.

The acid-base properties of these salts can be described by the following equilibrium:



For the  $\text{AlCl}_3$ -BPC system, the best value for the equilibrium constant appears to be  $1.2 \times 10^{-13}$  at  $40^\circ\text{C}$  [4]. An excess of  $\text{AlCl}_3$  promotes formation of  $\text{Al}_2\text{Cl}_7^-$  and results in an acidic solution. Solutions with less than 50 mole %  $\text{AlCl}_3$  are basic and a 1:1 mixture is neutral.

Another class of room temperature molten salts was reported in 1963 by Yoke and co-workers [5]. Equimolar quantities of copper(I) chloride and triethylammonium chloride combine to give a light yellow oil of formal composition  $(\text{C}_2\text{H}_5)_3\text{NH}^+(\text{CuCl}_2^-)$ . The color is a result of an ultraviolet charge transfer band and is not due to contamination [6]. Other molten salts based on copper(I) and either trialkylammonium or trialkylphosphonium salts have been prepared. These liquid salts are extremely oxygen sensitive and darken rapidly if exposed to air.

Vibrational spectroscopy suggests that several copper chloride species are present in these solutions [6]. Porterfield and Yoke used visible spectroscopy to study metal chloride complexes in these Cu(I) liquid salts [7]. The results obtained were very similar to the results obtained by other workers in high temperature molten salt systems.

Although the Cu(I) liquid salts are not suitable for electrochemical studies [8], there have been several studies of inorganic compounds in  $\text{AlCl}_3$  based molten salts. These molten salts have several advantages over other solvent systems:



(a) Radical species are stabilized. The decamethyl ferrocene dication can be prepared electrolytically in  $\text{AlCl}_3/\text{BPC}$  and is stable for days under argon. However, addition of dried, redistilled acetonitrile destroys the compound [9].

(b) Certain compounds can be spontaneously oxidized simply by adjusting the melt to an acidic composition. Decamethylferrocene [9] and nickelocene [10] can both be oxidized to their corresponding cations in this manner.

(c) Uncommon oxidation states are found for some compounds. Molybdenum(III) and molybdenum(IV) are both stable in these salts [11].

(d) Due to the variable acidity, chloro complex formation can be studied. In basic melts, tetrahedral metal chlorides are found for  $\text{Co(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Fe(II)}$ ,  $\text{Fe(III)}$ ,  $\text{Ag(I)}$ , and  $\text{Cu(I)}$  [12]. In acidic melts the nature of coordination is not as well understood.  $\text{Co(II)}$  and other related dipositive 3d ions are believed to be octahedrally coordinated, but the nature of the ligand is not known [13].

Photochemical reactions can also be done in these molten salts. It has been shown that several iron(II) diimines can be photochemically oxidized to the corresponding iron(III) diimines with low intensity visible light [14]. For most of the complexes studied, almost 100% of the ferrous complex was converted to the ferric form.

One of the most recent applications of molten salts is in the area of photoelectrochemistry at semiconductor electrodes. Liquid salts offer advantages over both aqueous and aprotic solvents. The conductivity of these salts is fairly high and the semiconductors appear to be stable to corrosion for months. Cells have been tested using n-GaAs, n-InP, and n- $\text{TiO}_2$  [15]. Overall efficiencies of close to 2% have been obtained if the liquid salt is diluted with benzene (50% by volume). In a closely related development, it was found that oxidation of several species can be sustained on illuminated semiconductors at potentials much smaller than in the dark [16].

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# Transition Metal Complexes of Imido Ligands: Structure and Reactivity

Yun Chi

Literature Seminar

December 9, 1983

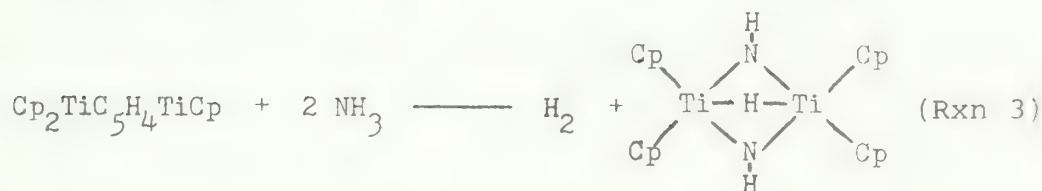
Transition metal complexes containing ligands in which there is M-N multiple bonding are currently the focus of considerable research activity [1,2]. Interest in complexes of imido (NR) ligands reflects growing recognition of their potential role in several areas, i.e., as synthetic reagents in organic chemistry [3,5], as intermediates in catalytic processes [6] and as analogs of oxo complexes [7,8].

In general, imido ligands are bound to transition metals in five different modes: terminal linear (1); terminal bent (2); symmetric doubly bridging (3); asymmetric doubly bridging (4) and triply bridging (5).



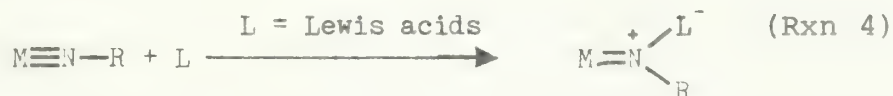
Doubly bridging imido ligands are symmetrically bound (3) for group IV transition metal dimers, e.g.,  $[(Me_2N)M]_2[\mu^tBuN]_2$ ,  $M = Ti, Hf, Zr$ , and unsymmetrically bound (4) for group VI metal dimers, e.g.,  $[(^tBuN)Me_2M]_2[\mu^tBuN]_2$ ,  $M = Cr, Mo, W$  [9]. The asymmetry of the bridging imido ligands in the later case, may be caused by second order Jahn-Teller effects. Triply bridging complexes (5) are symmetrically bound in trimetallic complexes, e.g.,  $H_2Os_3(CO)_9(NCH_3)$  [10].

Sharpless and coworkers have shown that the transition metal imido complexes,  $[Os(O)_n(NR)_{4-n}]$ ;  $n = 1, 2, 3$ , react stoichiometrically in vicinal hydroamination [3,4] (Rxn 1) and diamination reactions [5] (Rxn 2). An imido complex has been prepared directly from ammonia (Rxn 3) and has been found to be an olefin hydrogenation catalyst [11].





Terminal imido ligands have been shown to react with Lewis acids and bases. Lewis acids interact with the imido group through the nitrogen atom to form a zwitterionic adduct [12] (Rxn 4). However, bases react with the  $\alpha$ -hydrogen atom to produce alkylidene imido complexes [13] (Rxn 5). Schrock and coworkers have shown that terminal imido-alkylidene and imido-alkylidyne complexes are more stable than their oxo- analogs. Intermediates which are unstable in oxo-alkylidene chemistry can be isolated from the analogous imido complexes [13,14]. Thus, the imido ligand offer an opportunity to further the understanding of the alkylidene and alkylidyne chemistry.



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## Inorganic Bone-Imaging Agents

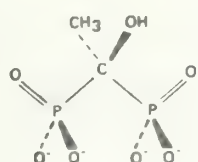
James R. Schwartz

Literature Seminar

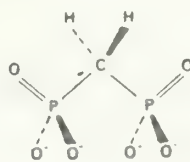
February 21, 1984

Inorganic radiopharmaceuticals [1] utilize complexes of chromium, iron, technetium, ruthenium, platinum, gallium, indium, and thallium. They possess chemical properties which allow localization at specific parts of the body. The resulting accumulations are traced by emitted radiation.

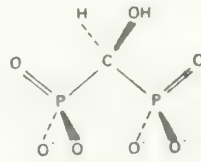
Technetium-99m ( $^{99m}\text{Tc}$ ) is the primary isotope used in nuclear medicine [2] for two reasons. First,  $^{99m}\text{Tc}$  has optimum nuclear properties for imaging, second the position of technetium in the periodic table ensures the possibility of generating wide ranges of complexes. An interesting application of  $^{99m}\text{Tc}$  is in the area of bone-imaging radiopharmaceuticals. To image bone,  $^{99m}\text{Tc}$  is most often chelated to a class of ligands known as diphosphonates:



HEDP  
(1-hydroxyethylidene) DP



MDP  
methylene DP



HMDP  
hydroxymethylene DP

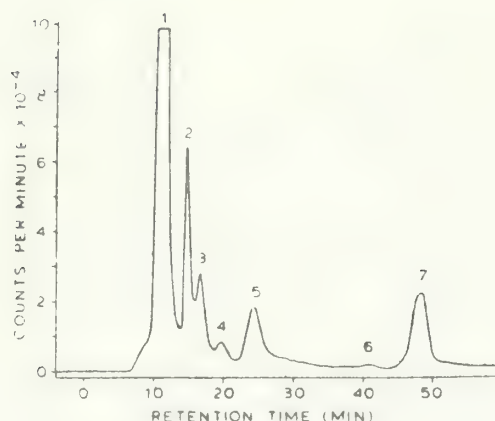
The preparation of Tc radiopharmaceuticals is based on the aqueous reduction of pertechnetate,  $\text{TcO}_4^-$ , in the presence of chelating agents which prevent the precipitation of  $\text{TcO}_2$ . The most commonly used reductant is stannous chloride. Evidence exists for a complicated reaction process which is dependent on reductant, ligand, pH, temperature, presence of oxygen, ligand-to-metal ratio, and reaction time.

Using stannous ion for reduction of  $\text{TcO}_4^-$  leads to several problems [3]. Since Sn(IV) and Tc(IV) have similar ionic radii, the incorporation of tin into the radiopharmaceutical may occur. For example, Deutsch et al. [4] have structurally characterized a bridged Tc-Sn-dimethylglyoxime complex. Also, the total amount of Sn(II) initially added to a radiopharmaceutical kit may not be in a usable form by the time  $^{99}\text{TcO}_4^-$  is added [5]. Side reactions involving tin will have a direct outcome on the final Tc oxidation state(s).

Electroanalytical techniques have been applied, with much difficulty, to the determination of Tc oxidation states. For example, Russell and Cash [6] have combined normal polarography, pulse polarography, and amperometric titrations to determine Tc oxidation states in aqueous media containing pyrophosphate, MDP, or HEDP.

To investigate the structure of the Tc-diphosphonates, Pinkerton et al. [7] developed an anion-exchange HPLC technique. When applied to  $\text{Tc}(\text{NaBH}_4)$ -HEDP and  $\text{Tc}(\text{NaBH}_4)$ -MDP preparations, at least seven components have been shown to be present [8,12]:





They concluded, based on the polymeric structure of  $[\text{Tc}(\text{OH})(\text{MDP})^-]_n$  [9], that the components represented various oligomers. It was also shown, both for HEDP [8] and MDP [10], that each separated component had different biodistributions.

Jurrisson et al. [11] have conducted *in vitro* experiments on the calcium affinity of coordinated diphosphonate ligands. A series of diphosphonate-cobalt complexes were titrated with calcium. The results from these experiments provided evidence for a relationship between structure and function of the ligands. They demonstrated that the nature of the groups attached to the carbon in the P-C-P backbone play an important role in calcium affinity.

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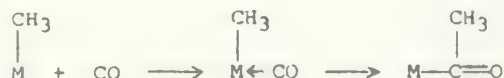
# Carbon Monoxide Activation by Actinides

Dean M. Millar

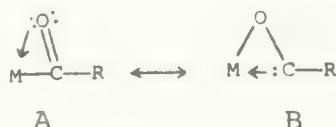
Literature Seminar

February 23, 1984

There is currently a great academic and industrial interest in understanding processes by which carbon monoxide (ultimately derived from coal) can be converted by various metal catalysts into useful organic compounds [1]. The mechanism of homogeneous transition metal CO activation is reasonably well understood and involves the migratory insertion of CO into a metal-carbon bond producing a metal acyl [2].

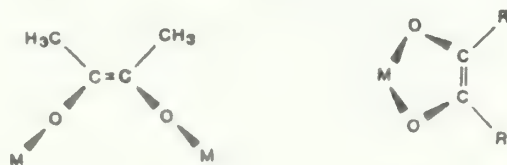


Classical acyl products of late transition metals show primarily only metal bonding to the acyl carbon. With early transition metals (Ti, Zr, Hf), however, significant bihapto acyl coordination of both the acyl carbon and oxygen is observed [3]. Nonclassical dihapto coordinated acyls have often been proposed as intermediates in the catalytic activation of CO. Intermediates such as these might be isolated by providing a metallic center with sufficient unsaturation and oxygen affinity to be stabilized by conjunctive metal-oxygen bonding.



The bis(pentamethylcyclopentadienyl) actinide complexes have three unique characteristics that lend themselves to nonclassical CO activation: high coordinative unsaturation, high kinetic lability, and high oxygen affinity [4]. The bonding in organoactinide acyls involves a major contribution from a carbene-like hybrid B due to the large magnitude of the metal-oxygen interaction. As a result, actinide acyls more closely resemble early transition metal acyls and have distinctly carbene-like chemical behavior.

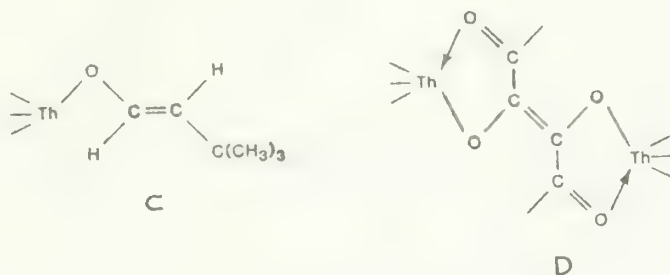
Actinide dimethyl complexes, as well as sterically unhindered actinide hydrides, react rapidly with CO to produce, quantitatively, both dimeric and monomeric complexes containing the cis-2-butene-2,3-diolate ligand [5].



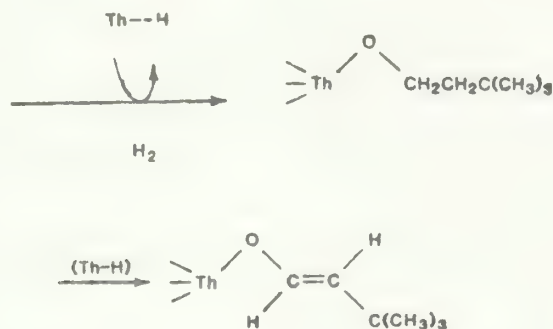
A mechanism for enediolate formation consistent with spectroscopic and kinetic data involves the insertion of the oxycarbene into an actinide hydride followed by a second CO insertion, hydrogen migration, and carbon-carbon bond formation [6].



Monomeric actinide  $\eta^2$ -acyls undergo reactions similar to the classical 1,2-hydrogen migration to produce the trans-eneolate ligand C, as well as reacting with an additional equivalent of CO to produce an enedionediolate ligand D [8].



The carbene-like reactivity of actinide  $\eta^2$ -acyls can be further exploited catalytically to produce hydrogenated products of the inserted CO [9]. Actinide acyls react with  $H_2$  in the presence of actinide hydrides to yield the corresponding alkoxide. When no  $H_2$  is present the hydrides catalyze the production of the trans-eneolate ligand.



Deuterium labeling studies detail a mechanism involving formal insertion of the carbenoid acyl carbon into a hydride bond, followed by  $\beta$ -hydrogen elimination to yield the trans-eneolate or in the presence of  $H_2$ , the alkoxide product. These reactions further underscore the oxycarbene character of organoactinide  $\eta^2$ -acyls and demonstrate that their nonclassical carbene-like reactivity can be used to produce homometallic hydrogenation and rearrangement processes.



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## Resonance Raman Studies of Heme Proteins and Models

Hye Kyung Cho

Literature Seminar

February 28, 1984

There has been considerable interest in heme proteins for many years. Even so, the electronic and structural changes associated with oxygen binding or electron transfer have not been determined unequivocally [1]. These problems are difficult since biological materials are very complex, thereby necessitating the use of highly sensitive spectroscopic probe which selectively sample the atoms in the vicinity of the active site. Resonance Raman (RR) spectroscopy offers considerable promise in this regard, if the atoms in the site rise to an isolated electronic absorption band [2]. RR spectroscopy has been extensively applied to heme proteins and metalloporphyrin analogues. By using RR, the chief obstacle encountered with biological materials, complexity, is almost totally solved.

Raman spectra are observed when light is scattered inelastically by molecules in solid, gases or liquids. In Raman spectroscopy a molecule is excited by a laser, light is scattered, and the energies of the inelastically scattered photons are analyzed. Raman and RR spectroscopies measure the frequency difference from the exciting line. These frequency differences correspond to vibrational transitions. The Raman and RR range cover the same region as the so-called middle-to-far IR, falling between visible and microwave light [3].

The total intensity of radiation scattered during a Raman process is proportional to the fourth power of the frequency shift and the second of the molecular polarizability or scattering tensor [4]. Raman, i.e., non-resonance Raman, mainly gets its intensity by the frequency shift of the incident radiation. The contribution of polarizability in Raman intensity is very small. However, as the laser exciting frequency in Raman approaches an allowed electronic transition in the molecule being investigated, those normal modes that are vibronically active in the electronic transition exhibit a pronounced enhancement ("resonance") in their Raman intensity.

For example, when a heme protein is irradiated in the region associated with porphyrin localized  $\pi \rightarrow \pi^*$  electronic transitions, the porphyrin vibrational mode intensities are enhanced by vibronic coupling. Generally, the Soret band excitation enhances the  $A_{1g}$  vibrational modes and  $\alpha$  or  $\beta$  excitation enhances non-totally symmetric vibrational modes, i.e.,  $B_{1g}$  and  $B_{2g}$  for porphyrin systems. Asymmetric vibrational modes,  $A_{2g}$  in porphyrin systems, show anomalous scattering with a depolarization ratio approaching infinity; these modes are inactive in normal Raman spectra [5].

A number of heme proteins and model systems have been the subject of recent studies and reviews [2,6]. RR was used first by Spiro et al. to characterize heme proteins [5]. Correlations were established between the frequencies of some prominent RR bands and the spin and oxidation states of the iron atom in protoporphyrin IX and in mesoporphyrin. Four bands were identified which offer promise as



oxidation and/or spin state makers [7]. Reduction of Fe(III) to Fe(II) leads to a small general lowering of frequencies, while much larger decreases accompanying conversion from low- to high-spin state. The former trend was explained in terms of changes in  $\pi$  back-donation, while the latter trend was attributed to structural changes accompanying the spin state change [8]. By spin and oxidation state markers, oxyhemoglobin was classified as a low-spin Fe(III) heme [7,8]. FeTPP (meso-tetraphenyl porphine) was studied in order to correlate frequency as a function of electronic and structural changes [9,10]. Mansuy et al. found four oxidation and/or spin state marker bands of Fe-TPP complexes and a characteristic band for pentacoordinated derivatives [9]. Since mainly in-plane porphyrin modes are enhanced by RR, all these correlation diagrams used in-plane porphyrin ring modes.

Burke et al. studied the oxyhemoglobin model compound, [Fe(O<sub>2</sub>)-(1-MeIm)(TpivPP)], Mono(N-methylimidazole)(dioxygen)meso-tetra-( $\alpha,\alpha,\alpha,\alpha$ -o-pivalamide-phenyl)porphinato iron(II), which has an end-on bent O<sub>2</sub> geometry from x-ray structure [11]. The close similarity of Fe-O<sub>2</sub> in the model compound and in oxyhemoglobin [12] was established by RR and IR. From this similarity they claimed that oxyhemoglobin has the same bent end-on Fe-O-O geometry and appreciable multiple bond character for the Fe-O<sub>2</sub> bond from its relatively high Fe-O<sub>2</sub> stretching frequency [10].

An RR line at 216 cm<sup>-1</sup> distinguishing the two quaternary structures of Hb, mainly T (low oxidation affinity) and R (high oxidation affinity) state, was found by Kitagawa et al. and was assigned to the Fe-N (HisF8) stretching mode. The  $\overline{\text{Fe-N}}$  frequency shift in the R and T transition was interpreted in terms of the tension model of Hb cooperativity [13]. N-Fe stretching in model compound such as Fe(II) picket-fence porphyrin and Fe(II) protoporphyrin IX has also been studied [14].

Recently, influences on the RR frequencies of heme proteins have been studied attributed to more subtle structural changes, such as globin [8] and vinyl-substituent effects [15], axial  $\pi$ -ligand effects [6], and porphyrin core size effects [16].

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# The Manganese Center in Photosynthetic Oxygen Evolution

Hsiu-Rong Chang

Literature Seminar

March 1, 1984

Photosynthetic oxidation of water to dioxygen is a process essential for the maintenance of life. The structure and mechanism of the enzyme which catalyzes the four-electron oxidation of two water molecules to dioxygen by photooxidation is being pursued in several laboratories.

For many years it has been known that manganese ions are required in oxygen-evolving photosynthesis organisms [1]. Removal of manganese from chloroplasts invariably results in the loss of their oxygen-evolving capacity. Manganese is attractive as an element in the water splitting reactions of photosynthesis because it has several stable oxidation states which encompass a wide range of redox potentials. However, the details of its participation have not yet been well established. It is generally agreed that "pools" of manganese exist in chloroplasts. These pools have been classified into three groups [2] only two-thirds of which are involved in O<sub>2</sub>-evolution.

In 1970 Kok et al. [3] proposed the first detailed scheme for the evolution of O<sub>2</sub> in photosystem II (PSII). In this scheme, the reaction center of PSII goes through four consecutive photoactive states (S<sub>0</sub>, S<sub>1</sub>, ..., S<sub>4</sub>), which are related by one electron oxidation (Figure 1). Oxygen is released at the decay of a final state

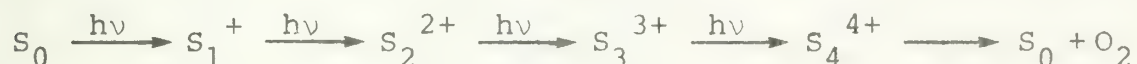


Figure 1

(S<sub>4</sub>) to the initial state (S<sub>0</sub>). The deduction that there is an accumulation of oxidizing equivalents at the poly-manganese site in the oxygen-evolving system has initiated several attempts to demonstrate experimentally changes in the oxidation state of manganese. The dependence of the NMR relaxation times of water protons on the number of light flashes given to chloroplasts was taken by Whydrzynski et al. [4] as evidence for changes in the oxidation state of photosynthetic manganese. Support for the oxidation state changes has also been obtained by Sauer et al. [5,6]. In their work, the amount of manganese released after heat-treatment of flash-illuminated chloroplasts was estimated. Recently, Dismukes et al. [7,8] have been able to observe a multi-line EPR signal due to hyperfine structure from two or more manganese ions by a freeze-trapping technique. This signal is similar to that seen [7,8] for the Mn<sup>III</sup>Mn<sup>IV</sup> complex (bpy)<sub>2</sub>Mn<sup>III</sup><O>Mn<sup>IV</sup>(bpy)<sub>2</sub><sup>3+</sup>. EXAFS studies of the manganese ions in PSII further suggest a Mn-Mn separation of 2.7 Å and an inner coordination sphere for the metal ions consisting of "light" donor atoms (O and N) [9,10]. Several mechanisms have been proposed for the oxygen evolution reaction in the Mn center of PSII. One of the mechanisms is shown in Figure 2.



Recent studies of a Mn(III)-catechol-semiquinone chelate system (i.e., Figure 3) suggest that system may serve as an important model for the O-O bond formation during the oxidation of water. The existence of the "quinoid" species has also been supported by Sauer's observation of a rapidly decaying ( $\tau = 400-900 \mu s$ ) radical species in spinach chloroplasts [11]. Recent work of Pierpont, Hendrickson and coworkers has demonstrated that quinone ligands are capable of functioning as multielectron storage sites during the process of producing oxygen from two coordinated water molecules [12].

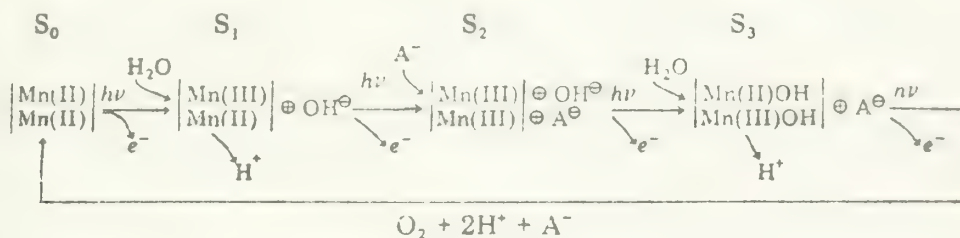
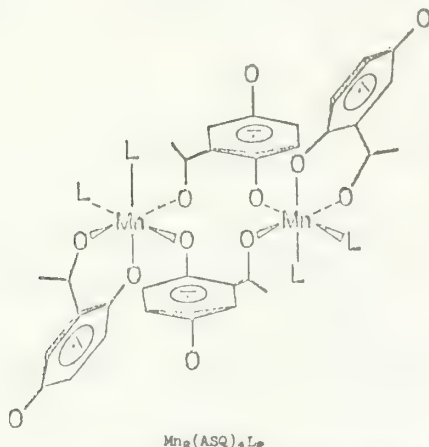


Figure 2



ASQ: 2-acetyl-1,4-benzosemiquinone

L: solvent

Figure 3



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# ENDOR - APPLICATIONS IN TRANSITION METAL CHEMISTRY

Ming Xie

Literature Seminar

March 8, 1984

To resolve the hyperfine and quadrupole interactions between unpaired electron and nuclear spins which are not accessible with EPR or NMR, Feher introduced a double resonance technique [1] called Electron Nuclear Double Resonance (ENDOR). In the ENDOR experiment, an EPR transition, the so-called observer, is partially saturated, and a radio frequency field, the so-called pump, is swept in the region of the nuclear resonance transition. The change in the EPR signal is monitored over the rf frequency. The principle of ENDOR is shown for a  $S=1/2$  and  $I=1/2$  system in Figure 1. The bottom two spectra a and b correspond to  $\nu_n > A/2$  and  $A/2 > \nu_n$ , respectively.

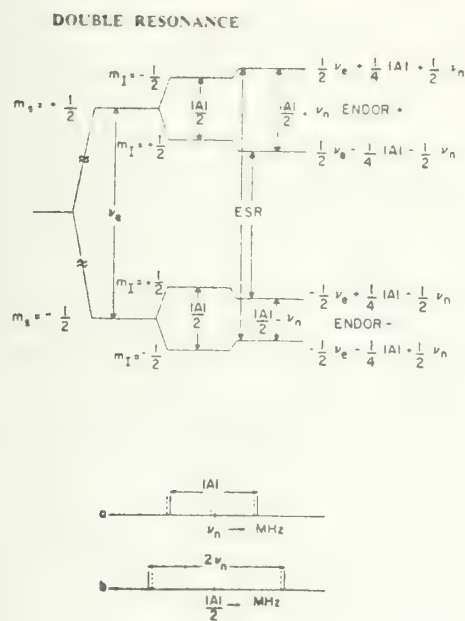


Figure 1

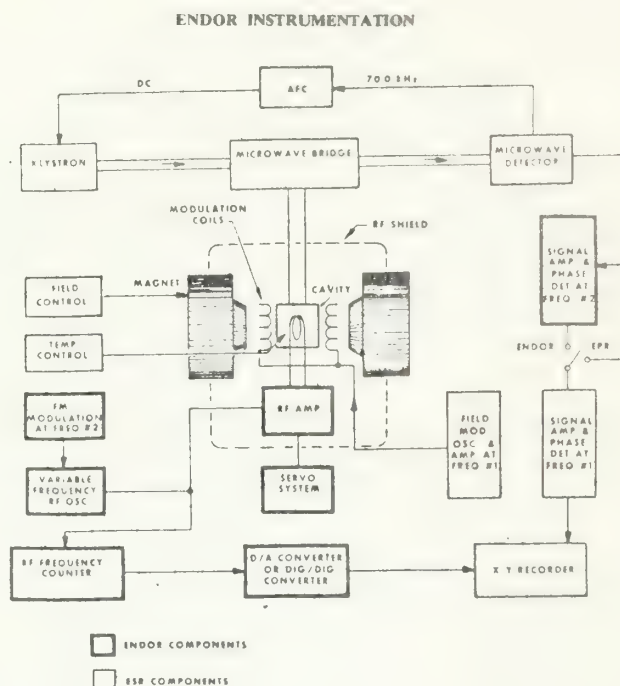


Figure 2

An ENDOR spectrometer is an EPR spectrometer with an extra rf system. The block diagram in Figure 2 shows the difference between these two spectrometers. In low power ENDOR spectrometer, the rf power is usually below 1W. On the other hand, the rf power employed by a high power spectrometer can range from 10W to 100W. In DOUBLE ENDOR, two independently tunable rf fields are mounted in the ENDOR cavity.

While solution ENDOR has been widely used to study organic free radicals, only one such study on transition metal complexes has so far been published [2]. It was found that the eight protons of chromyl ethyleneglyconate anion are equivalent with isotropic hyperfine coupling of 1.74 MHz. In addition, the authors studied the microwave, rf field and temperature dependence of the ENDOR



signal amplitude and line width. The majority of ENDOR experiments on transition metal complexes have been done on solids or glasses. In the first extensive ENDOR study of a transition metal complex, Rist and Hyde [3] applied ENDOR to Cu-8-hydroxyquinolate substituted into a single crystal and a powder of phthalimide. They successfully determined the hyperfine and quadrupole tensors by studying the angular dependence of the spectra. They found that it is possible to obtain single-crystal-like spectrum which corresponds to a restricted orientation, with powder or frozen glass samples. This orientation selection technique has now been generally adopted [4,5].

Of biological systems, hemoglobin (Hb) and myoglobin (Mb) have been the most extensively studied with the ENDOR technique [6]. It has been found that the two high frequency peaks of the proximal histidine nitrogen in Mb-F are about 0.5 MHz lower in frequency than the corresponding transitions in aquo-Mb. This shift is resulted from the trans effect upon the replacement of  $H_2O$  by  $F^-$ . Recently, Hoffman applied ENDOR to the nitrogenase MoFe protein and found molybdenum to be correlated to the  $S=3/2$  center [7].

ENDOR induced EPR (EI-EPR) is a convenient method to separate overlapping EPR signals from different radicals, molecular conformations or magnetic sites. In EI-EPR the external field  $B_0$  is swept, and the NMR transition is saturated as a selector. Rudin and co-workers found that single-crystal-like EPR can be obtained with a powder sample by using the EI-EPR technique [8].

Two types of TRIPLE resonance (DOUBLE ENDOR) have been developed [9]. In the so-called "general" TRIPLE, the EPR transition and one of the NMR transitions are partially saturated. The intensity change in single ENDOR is observed while the second rf field is swept. Whereas, in "special" TRIPLE both rf fields are swept simultaneously and symmetrically with respect to the free nuclear resonance transition frequency. General TRIPLE is usually applied to determine the relative signs of hyperfine constants from different nuclei [10]. In special TRIPLE the spectrum amplitude is directly proportional to the number of the nuclei which have the same hyperfine constant. TRIPLE resonance has been used by several authors to study transition metal complexes. Kirste recently showed that TRIPLE resonance can be used to reduce a powder ENDOR spectrum to a single-crystal-like one [11].

In the last few years, ENDOR has shown rapid developments in the following aspects:

1. Increase in its resolution ability by using special rf sources.
2. Increase in its intensity by developing higher power rf frequency field.
3. Time-domain ENDOR.

The ENDOR technique, of course, is not restricted to transition metal complexes. A fast growing interest in double and multiple resonance is noticed in other fields such as radicals, radiation and polymer chemistry, solid state physics, etc. [12,13].





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## Three-Iron Clusters in Iron-Sulfur Proteins

Sten A. Wallin

Literature Seminar

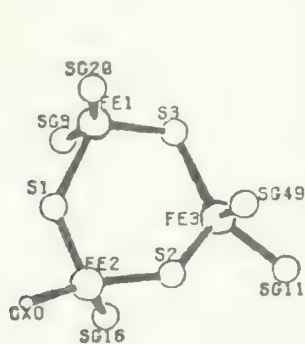
March 27, 1984

The existence of [3Fe-xS] clusters [1] was first postulated in late 1979/early 1980 based on a combined EPR and Mössbauer study of the *Azotobacter vinelandii* ferredoxin I (A.v.Fd) [2] and an x-ray crystallographic study of A.v. Fd [3]. Shortly thereafter, this rather convincing evidence for a novel Fe/S cluster type was corroborated by the results of EPR and Mössbauer studies on *Desulfovibrio gigas* Fd II (*D. gigas* Fd II) [4] and beef heart mitochondrial aconitase [5]. At the present time, at least a dozen "native" proteins (*i.e.*, obtained upon ordinary aerobic purification) have been shown to contain 3Fe clusters with an additional dozen displaying some of the characteristic features of this cluster type.

Mössbauer spectroscopy provides convincing evidence for the presence of 3Fe clusters [6]. Other spectroscopic probes that exhibit signals characteristic of [3Fe-xS] sites are low temperature magnetic circular dichroism [7], low temperature resonance raman [8] and the linear field effect in EPR [9].

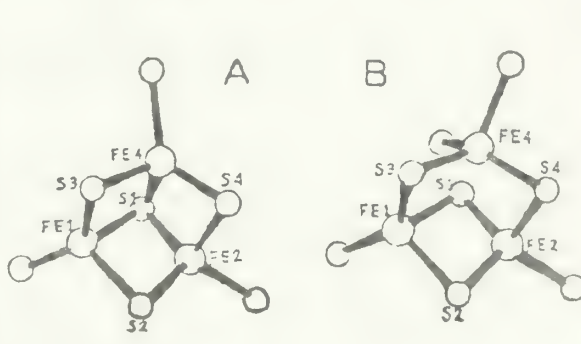
The subject of 3Fe cluster containing proteins has had more than its share of controversy. By late 1981/1982, it had been demonstrated that, in a number of cases, 3Fe clusters are definitely man-made artifacts. For example, oxidation of certain native [4Fe-4S]<sup>2+,+</sup> ferredoxins with Fe(CN)<sub>6</sub><sup>3-</sup> yields not the expected [4Fe-4S]<sup>3+</sup> oxidized HiPIP state, but rather, a [3Fe-xS] species [10,11]. In other systems, 3Fe clusters can be converted, under appropriate conditions, into [4Fe-4S] clusters with or without the addition of Fe<sup>2+</sup> or S<sup>=</sup> [5,12,13,14].

Another area of some controversy concerns the structure(s) of 3Fe clusters. Stout's 2.5 Å resolution x-ray crystallographic analysis of A.v. Fd (a 7Fe protein) showed, in addition to a conventional [4Fe-4S] site, a planar, twist-boat six-membered ring [3Fe-3S] structure with d<sub>Fe-Fe</sub> = 4.1 Å [3,15]. In contrast, Fe EXAFS studies on *D. gigas* Fd II [16] and aconitase [12] clearly indicate a much more closed cluster structure with d<sub>Fe-Fe</sub> = 2.7 Å.



[3Fe-3S]

$$d_{\text{Fe-Fe}} = 4.1\text{\AA}$$



[3Fe-4S]

$$d_{\text{Fe-Fe}} = 2.7\text{\AA}$$



Earlier studies on the activation of inactive "native" aconitase suggested a [3Fe-4S] cluster for aconitase [5,12,13]. This has been confirmed by a recent high-precision determination of the Fe/S<sup>2-</sup> stoichiometry showing that "native" aconitase contains  $2.9 \pm 0.2$  Fe/molecule and  $3.9 \pm 0.2$  S<sup>2-</sup>/molecule [17]. Very recently, it has been shown that the Fe EXAFS of [4Fe-4S] depleted *A.v.* Fd (*i.e.*, containing only the 3Fe cluster) is virtually identical to that of "native" aconitase [18].

On the basis of the above, as well as on the strong similarity of the RR spectra for all studied [3Fe-xS] proteins and the results of normal mode calculations for various 3Fe cluster geometries [19], it has been suggested that all 3Fe clusters are of a "closed" (*i.e.*, d<sub>Fe-Fe</sub> = 2.7 Å) [3Fe-4S] form.

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# Synthesis and Reactivity of Cluster Bound Acetylides

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Literature Seminar

April 26, 1984

There has been a great deal of study on the synthesis, bonding, structure, and reactivity of the alkyne transition metal complexes [1]. In particular, cluster bound acetylides ( $\text{RC}\equiv\text{C}-$ ) have recently provided some interesting chemistry. The acetylide, which is related to  $\text{C}\equiv\text{O}$  and  $\text{C}\equiv\text{N}$  in its coordination chemistry, has a variety of bonding modes (e.g.,  $\mu-\eta^2$ ,  $\mu_3-\eta^2$ ,  $\mu_4-\eta^2$ ) in clusters. The interaction of the acety-



$\mu-\eta^2$



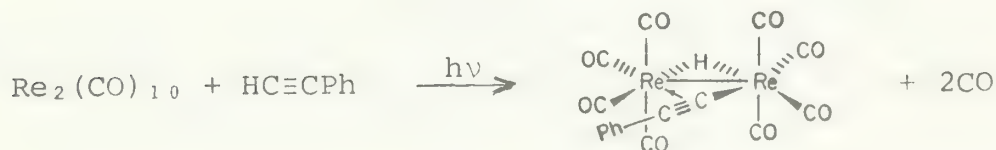
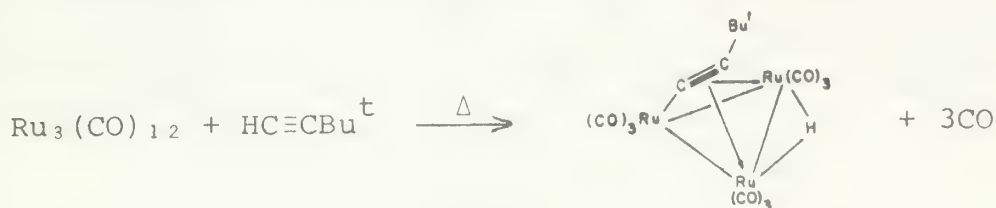
$\mu_3-\eta^2$



$\mu_4-\eta^2$

lide with metal atoms reveal unusual and possibly useful patterns of chemical reactivity.

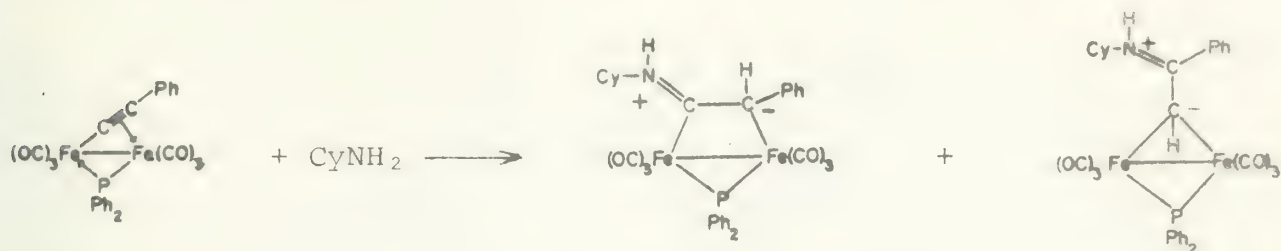
The acetylide complexes are synthesized by substitution of carbonyl groups in metal carbonyl clusters with alkynes [2]. The carbonyl substitution reaction proceeds thermally or in the presence of  $\text{Me}_3\text{NO}$  in most cases and photochemically in a few cases. Thermal reaction of  $\text{Ru}_3(\text{CO})_{12}$  with  $\text{HC}\equiv\text{CBu}^t$  produces  $(\mu-\text{H})\text{Ru}_3(\text{CO})_9(\mu_3-\eta^2-\text{C}\equiv\text{CBu}^t)$  [3]. Dirhenium decacarbonyl  $\text{Re}_2(\text{CO})_{10}$  reacts photochemically with  $\text{HC}\equiv\text{CPh}$  to yield  $(\mu-\text{H})\text{Re}_2(\text{CO})_8(\mu-\eta^2-\text{C}\equiv\text{CPh})$  [4].



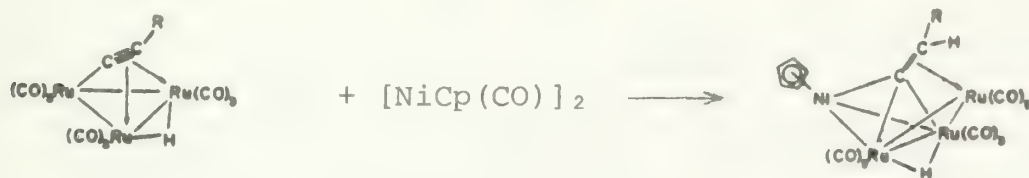
The reactivity of acetylide complexes has been studied with a variety of nucleophiles and electrophiles. Isomerization and hydrogenation have also been investigated.



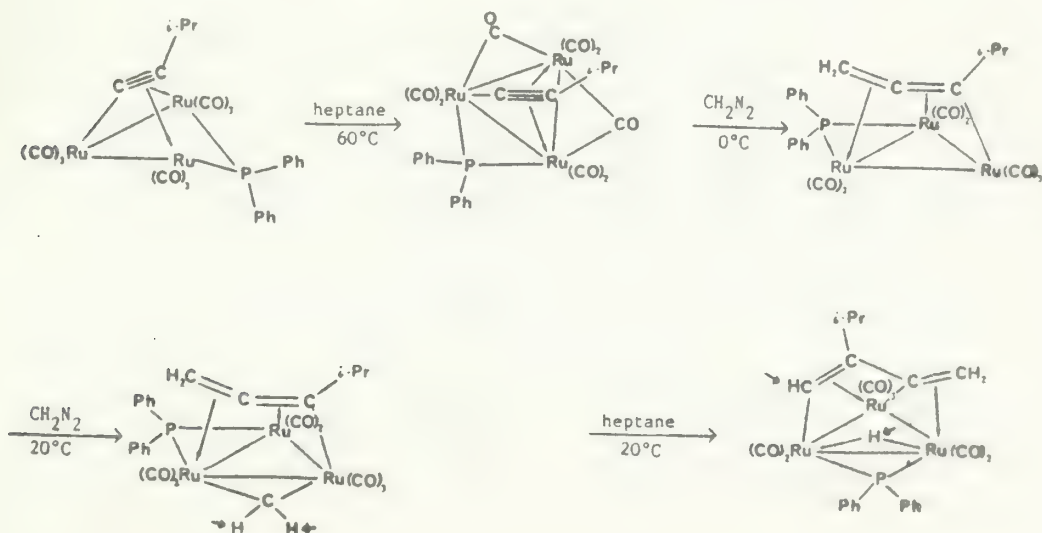
The nucleophilic reactions of  $\mu\text{-}\eta^2$  acetylide  $(\mu\text{-pph}_2)\text{Fe}_2(\text{CO})_6\text{-}(\mu\text{-}\eta^2\text{-C}\equiv\text{CPh})$  with amines, phosphines, phosphites, and isonitriles give adducts which have zwitterionic structures with the nucleophilic atoms attached to the original  $\alpha$ - or  $\beta$  acetylenic carbon [5].



The  $\mu_3\text{-}\eta^2$  acetylides  $(\mu\text{-pph}_2)\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CPh})$  and  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9\text{-}(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CPh})$  also react with nucleophiles [6]. The regioselectivity of nucleophilic attack depends on the electronic and steric properties of the group R and incoming nucleophiles. Under certain conditions, nucleophilic attack causes carbonyl substitution. For  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9\text{-}(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CBu}^t)$ , reactions with phosphites and phosphines yield only substitution products of the type  $(\mu\text{-H})\text{Ru}_3(\text{CO})_8(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CBu}^t)(\text{L})$  [7]. Carbonyl substitution occurs regioselectively on the ruthenium atom  $\sigma$  bonded to the acetylide. The metallic nucleophile such as  $[\text{NiCp}(\text{CO})]_2$  reacts with  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CPr}^i)$  to yield a mixed metal vinylidene cluster  $(\mu\text{-H})(\eta^5\text{-C}_5\text{H}_5\text{Ni})\text{Ru}_3(\text{CO})_9(\mu_4\text{-}\eta^2\text{-C}=\text{CHPr}^i)$  [8].



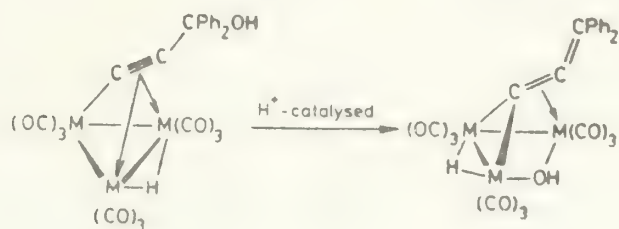
Acetylides also react with electrophilic acetylenes and diazomethane to yield products in which carbon-carbon bonds have formed [9]. Diazomethane, which is known to be a carbene precursor, reacts with  $(\mu\text{-pph}_2)\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CPr}^i)$  to give  $(\mu\text{-H})(\mu\text{-pph}_2)\text{Ru}_3(\text{CO})_7(\mu_3\text{-}\eta^4\text{-CH}_2=\text{C}=\text{CCPr}^i)=\text{CH})$  via the allenyl complex  $(\mu\text{-pph}_2)\text{Ru}_3(\text{CO})_8(\mu_3\text{-}\eta^3\text{-CH}_2=\text{C}=\text{CPr}^i)$  [10].







Acid induced isomerization of  $(\mu\text{-H})\text{M}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CCPh}_2\text{OH})$ , ( $\text{M}=\text{Ru}, \text{Os}$ ), involves hydroxide transfer from carbon to metal atoms [11]. This reaction may be regarded as an intramolecular oxidative addition



of an alcohol with carbon-oxygen bond cleavage. Hydrogenation of  $(\mu\text{-pph}_2)\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CBu}^t)$  gives  $\text{CH}_2=\text{CHBu}^t$  and the coordinatively unsaturated cluster  $(\mu\text{-H})\text{Ru}_3(\text{CO})_9(\mu\text{-pph}_2)$  [12].

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# Synthetic Iron Porphyrins as Models for Heme Proteins

Daniel R. English

Final Seminar

May 29, 1984

Iron porphyrins are a ubiquitous active site in biological systems [1]. This is due to the ability of the robust porphyrin macrocycle to stabilize iron in at least four oxidation states and six spin states [2]. Impetus for the study of iron porphyrins lies in the desire to understand how they work such chemical magic as shape selective oxidations [3] and oxygen transport and storage [4].

Initial efforts were aimed at understanding how axial ligation controls the oxidation chemistry of single-atom-bridged dimers. This led into a study of a complex which is capable of reversibly interacting with dioxygen in frozen glass media. Attempts to extend the pantheon of single-atom-bridged dimers to sulfur resulted in the synthesis and characterization of the first low-spin five-coordinate ferric porphyrin thiolate.

$(\text{FeTPP})_2\text{O}$ , where TPP is the dianion of tetraphenylporphyrin, contains two high-spin ferric atoms [5]. Oxidation of this complex to the dication occurs on the porphyrin rings yielding porphyrin pi-cation radicals [6]. This behavior can be contrasted with the isoelectronic complexes  $(\text{FeTPP})_2\text{N}^+$  and  $(\text{FeTPP})_2\text{C}$ . These species are oxidized at iron yielding Fe(IV) complexes [7,8]. The results can be rationalized in terms of relative electronegativities and pi-bonding abilities.

$(\text{FePor})_2\text{N}^+$  complexes (where Por can be a number of tetra-arylporphyrins) can be further oxidized to yield  $(\text{FePor})_2\text{N}^{2+}$ , a stable iron(IV) porphyrin pi-cation radical. These nitride-bridged systems are the only such complexes which are stable at room temperature to date. The electronic structure of these species is dependent on the counterions and porphyrin substituents. For example,  $[(\text{FeTPP})_2\text{N}](\text{SbCl}_6)_2$  has the pi-cation-radical localized on one porphyrin ligand, while  $[(\text{FeTPP})_2\text{N}](\text{CF}_3\text{SO}_3)_2$  has the radical delocalized over both of the porphyrin ligands. These results indicate that nitride is able to stabilize highly oxidized iron porphyrins. This reinforces the theory that highly-charged axial ligands capable of forming strong pi-bonding interactions are necessary to stabilize highly oxidized biological intermediates [4].

$(\text{FeTPP})_2\text{N}$  was reported to bind pyridine in a polar frozen glass medium [9]. Further investigation of this phenomenon revealed that the presence of dioxygen was responsible for the alteration of the EPR signals of the dimer [10]. The reaction with oxygen is totally reversible. The oxygen adduct has been studied by a battery of physical techniques. The optical spectrum of the oxygen adduct is equivalent to that of the lone dimer; this indicates that the interaction is quite weak. Mössbauer spectra demonstrate that the iron atoms are inequivalent in the adduct while EPR data indicate a less anisotropic g tensor and appreciably diminished  $^{14}\text{N}$  and  $^{57}\text{Fe}$  hyperfine coupling relative to the nonadducted species.  $\text{O}_2$  titrations, as monitored by EPR,





show that the adduct's stoichiometry is one O<sub>2</sub> per dimer. All these data are consistent with a weak axial interaction of O<sub>2</sub> with one side of the  $\mu$ -nitrido dimer. This is the first report of the reversible interaction of O<sub>2</sub> with a ferric porphyrin.

To date, synthetic five-coordinate ferric porphyrin thiolates are all high-spin [11,12,13]. Reaction of S<sub>8</sub> and LiB(Et)<sub>3</sub>H with Fe(TAP)Cl, where TAP is the dianion of p-methoxyphenylporphyrin, produces Fe(TAP)SH. The product is a low-spin ferric species as indicated by the following data: The magnetic moment corresponds to an S=½ system. A toluene glass of Fe(TAP)SH gives an EPR spectrum with g values of 3.9 and 1.7 at 4K. The Mössbauer spectrum consists of a single doublet with an isomer shift and quadrupole splitting similar to that of other low-spin ferric complexes [14]. The pyrrole proton resonance at -19 ppm is typical of low-spin iron porphyrins [15]. Splitting of the ortho and meta resonances is consistent with five-coordination. The stereochemistry of Fe(TAP)SH has been determined by a single-crystal x-ray structure. The average Fe-N<sub>por</sub> distance of 2.01 Å is indicative of a low-spin iron center [2].

Fe(TAP)SH represents a new class of porphyrins relevant to heme enzymes containing sulfur ligation, such as chloroperoxidase (CPO) and cytochrome P-450. While thiolate ligation has been demonstrated for cytochrome P-450 [16], EPR studies suggest that CPO has an axial ligand with similar electron-donating properties that is not thiolate [17]. The EPR characteristics of CPO are reproduced most faithfully by the HS<sup>-</sup> adduct of hemoglobin [17]. The isolation of Fe(TAP)SH indicates that exogenous sulfur may be a realistic alternative to thiolate axial ligation in CPO.

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# Alkyl, Alkylidene and Alkylidyne Triosmium Chemistry

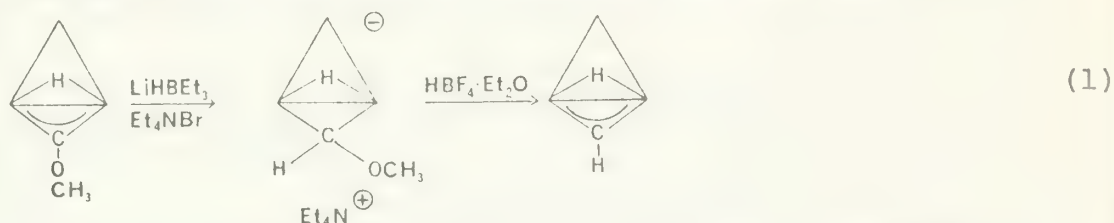
Michelle Cree-Uchiyama

Final Seminar

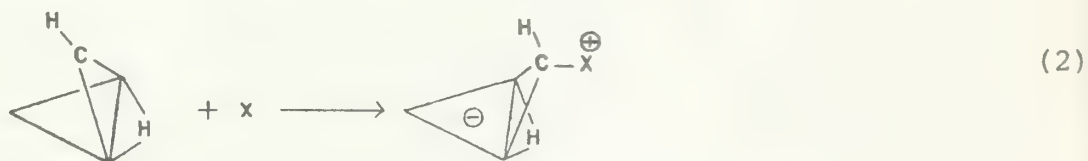
June 7, 1984

Recent interest in the chemistry of polynuclear metal complexes results from proposals suggesting these clusters may serve as models for metal surfaces [1]. Cluster bound alkyl, alkylidene, and alkylidyne groups are of particular interest due to their implicated role in the hydrogenation of carbon monoxide and related processes catalyzed by metal surfaces [2].

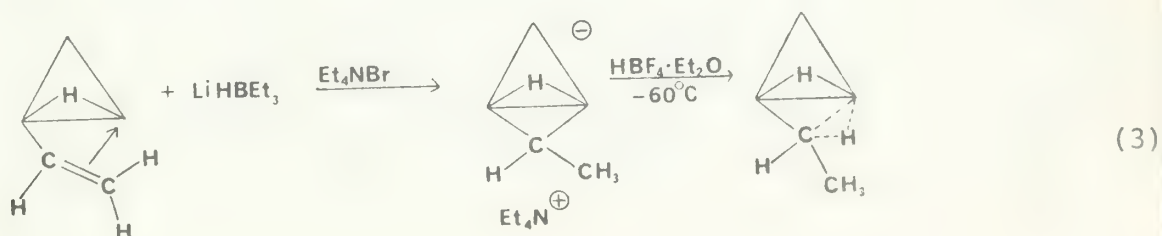
$\text{HOs}_3(\text{CO})_{10}\text{CH}$ , a new complex with a triply bridging methylidyne has been prepared (eq. 1). In contrast with previous examples the methylidyne ligand in this complex interacts much more strongly with two of the metal centers than the third.  $\text{HOs}_3(\text{CO})_{10}\text{CH}$  has been



characterized by an X-ray crystal structure by Churchill and Bueno [3].  $^{13}\text{C}$  NMR data for  $\text{HOs}_3(\text{CO})_{10}\text{CH}$  in solution are fully consistent with the solid state structure. Bonding in the methylidyne complex may be regarded as two-electron donation from the formally saturated  $\text{Os}(\text{CO})_4$  center to the electrophilic carbon atom of the bridging  $\text{CH}$  moiety. The facile reactions of  $\text{HOs}_3(\text{CO})_{10}\text{CH}$  with various nucleophiles provide further evidence for the electrophilic nature of this methylidyne ligand.



Bridging alkyl derivatives of transition metal clusters are rare, yet their properties are potentially relevant to an understanding of Fischer-Tropsch and related processes involving C-H bond activation. Previously reported examples of  $\mu$ -alkyl complexes have not included alkyl groups which contain  $\beta$ -hydrogens, consequently, the study of their reactivity has been limited [4]. We have prepared a series of triosmium alkyls containing both  $\alpha$  and  $\beta$  hydrogens [5,6,7]. The synthesis of the simplest of these, the ethyl complex, is shown in equation 3.







The alkyl ligands contain  $\alpha$ -C-H-Os three-center two-electron bonds.  $^{13}\text{C}$  NMR spectra of the ethyl complex,  $\text{HOs}_3(\text{CO})_{10}(\text{CH}_2\text{CH}_3)$ , indicate the diastereotopic methylene hydrogens are equilibrated via a symmetric unsaturated intermediate, electronically analogous to  $\text{H}_2\text{Os}_3(\text{CO})_{10}$ . The alkyl ligands are subject to both  $\alpha$  and  $\beta$  elimination processes, the latter of which predominates at higher temperature. The addition of nucleophiles induces reductive elimination of the alkane.

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# Studies of Dielectric Relaxation in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ with

## Dielectric Time Domain Spectroscopy

Peter Doan

Final Seminar

July 20, 1984

Dielectric time domain spectroscopy is a technique used in measurements of dielectric loss functions in a range from 1 MHz to 3 GHz [1]. Real time response  $V(t)$  of a sample to short rise time electrical potential ( $\sim 50$  psec) are recorded and Laplace transformed to the frequency domain,  $v(i\omega)$ . The complex permittivity or dielectric response  $E^*(i\omega)$  in the frequency domain for an open coaxial line sample cell design is

$$\epsilon_{\sigma}^* - \epsilon_r^* = \frac{c}{d} \frac{v_r - v_s}{i\omega(v_r + v_s)} z \cot z \quad (1)$$

where the subscripts r and s represent reference and sample, c is the speed of light in a vacuum, d the effective electric sample depth, and  $z = \frac{(\omega d)}{c} (\epsilon_r^* + \epsilon_s^*)^{1/2}$ . (The  $i\omega$ 's of the functions are left off). The usual reference is air,  $\epsilon_{\text{air}}^* = 1$ . If the dielectric loss function fits to

$$\epsilon^* = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + i\omega\tau} = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + (\omega\tau)^2} - i \frac{(\epsilon_0 - \epsilon_{\infty})\omega\tau}{1 + (\omega\tau)^2}$$

the sample exhibits Debye dielectric behavior, which is associated with the rotation of dipoles.

Application of electric field to a dielectric solid with partially mobile charges creates an added form of polarization to those normally associated with solid state properties. At a local level, the movement of an anion or cation to a previously vacant defect site can be pictured as dipole motion. The first report of this was by Breckenridge in 1948 as a study of alkali halides [2]. Since then there have been theoretical justifications for the assumption of Debye-like dielectric behavior in these systems [3,4,5].

The  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$  systems are perovskites where the replacement of an  $\text{La}^{3+}$  with  $\text{Sr}^{2+}$  creates an  $\text{Fe}^{4+}$  for charge balance. Mössbauer studies [6] show the iron sites have an averaged oxidation state between +3 and +4 at room temperature because of thermal motion of the  $\text{Fe}^{4+}$  hole. Previous results on systems with  $0.1 \leq x \leq 0.3$  using TDS measured the thermal barriers to dielectric relaxation and conductivity and found  $\Delta E_D < \Delta E_{\text{con}}$ .

A signal averaging interface board attached to the time domain reflectometer (TDR) improved the accuracy and greatly speeded up the acquisition of results. Analysis of the spectra by equation 1 proved limited due to instrumental difficulties. The spectra are analyzed by simulation using a program designed to take Debye dielectric parameters,  $\epsilon_{\infty}$ ,  $\epsilon_0 - \epsilon_{\infty}$ , and  $\tau$ , produces  $V_s(t)$ . Results for  $\epsilon_{\infty}$





and any relaxation times less than 0.5 nsec are good, for  $0.5 \leq \tau \leq 1$  nsec they are marginal, and for longer  $\tau$  values, suspect at best.

Studies on systems with low dopant levels ( $x = 0.005, 0.01$ ) are done in order to determine the barriers to dielectric relaxation in systems where the defects are well separated. Both the 0.5% and 1% doped samples exhibit two distinct relaxation times at temperatures above 300K. The low frequency (long  $\tau$ ) relaxation has a larger loss ( $\epsilon_0 - \epsilon_\infty$  value) at temperatures between 300-340 in the 1% system but begins to drop at these temperatures. Analysis of the barrier gives a  $\tau_0$  value of 100 femtoseconds and a barrier of 0.22 eV. Estimates for the longer  $\tau$  relaxation gives  $\tau_0 = 50$  femtoseconds with the same barrier. In the 0.5% system the  $\tau_0$  and  $\Delta E$  values for the two relaxation times are 337 femtosec, 0.19 eV, 1.66 psec, 0.17 eV for the short and long frequencies, respectively.

No single reason is found for the behavior seen in these samples. Assigning a relaxation time to a certain phenomenon is difficult without more and better data. However, a mixture of the undoped  $\text{LaFeO}_3$  with the doped systems show the low frequency relaxation mechanism is affected more than the high frequency mechanism. This may point to the long  $\tau$  being associated with surface polarization rather than bulk effects or to conductivity in the sample. Results on the effects of particle size and packing density proved inconclusive.

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Primary Photoproducts and the Mechanism of Ligand Substitution  
in the Photochemistry of Dinuclear Metal Carbonyls

Thomas R. Herrinton

Final Seminar

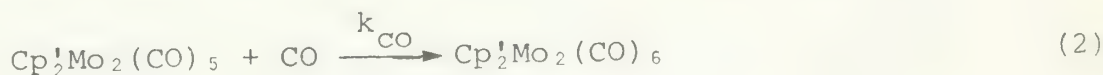
August 3, 1984

The photochemistry of dinuclear metal carbonyl compounds has been studied extensively in the past two decades. Nonetheless, the identities and reaction mechanisms of the primary photoproducts in the photolysis of these complexes have remained elusive. Early work indicated that metal-metal bond homolysis was the sole photo-process [1]. More recently loss of a CO ligand has been shown to occur in some systems [2,3,4]. In order to further the understanding of this problem a study of the photochemistry of bis(pentamethylcyclopentadienylmolybdenumtricarbonyl) ( $\text{Cp}_2^*\text{Mo}_2(\text{CO})_6$ ) was performed to determine its primary photoproducts.

Flash photolysis methods were used to investigate this question. High concentrations of the primary photoproducts are achieved by a brief ( $\text{FWHM} \approx 35 \mu\text{S}$ ) pulse of broad band irradiation, and then either the return of the original dimer or the disappearance of the transients can be monitored on the microsecond timescale by optical absorption spectroscopy. Observations of the return of the 495 nm absorbance band of  $\text{Cp}_2^*\text{Mo}_2(\text{CO})_6$  following the flash established the existence of two pathways for reforming the parent dimer. The first of these was quite rapid, followed second-order kinetics, and showed no dependence on  $[\text{CO}]$ . This process is proposed to be a radical recombination reaction (eq. 1).



The value of  $k_r$  is  $(8.0 \pm 0.6) \times 10^8 \text{M}^{-1}\text{s}^{-1}$ . The second, slower pathway followed first-order kinetics under a CO atmosphere, and the observed rate constant did depend on  $[\text{CO}]$ . Consequently, it is proposed that the second pathway involves CO recapture as shown in equation (2).



The value of  $k_{\text{CO}}$  is  $(4.4 \pm 0.4) \times 10^3 \text{M}^{-1}\text{s}^{-1}$ .

Examination of the optical spectrum from 560-800 nm reveals two transients with overlapping absorbance bands. One of these decays rapidly by second-order kinetics, and is believed to be  $\text{Cp}^*\text{Mo}(\text{CO})_3 \cdot$ . This is the first spectroscopic observation of a molybdenum-based metal carbonyl radical at room temperature. The second transient's absorbance disappears by pseudo-first-order kinetics at the same rate as found in equation (2). This absorbance is assigned to  $\text{Cp}_2^*\text{Mo}_2(\text{CO})_5$ .



Not all of the original absorbance at 495 nm is restored by these two processes. Some absorbance loss remains for several minutes, although it is all recovered eventually under a CO atmosphere. This slow process is proposed to be the carbonylation reaction shown in eq. (3).



Equation (3) is a known reaction [5]. A combination of flash and continuous photolysis experiments determined that the triply-bonded dimer is formed by loss of CO from  $\text{Cp}^{\dagger}\text{Mo}(\text{CO})_3\cdot$  and subsequent radical coupling. Given this fact, the percentage of photolyzed  $\text{Cp}_2^{\dagger}\text{Mo}_2(\text{CO})_6$  molecules which undergo CO loss was calculated to be 10%.

The reaction pathways which are utilized by primary photoproducts have also been a subject of controversy. For example, both dissociative [6] and associative [7] mechanisms have been proposed for ligand substitution of  $\text{Mn}(\text{CO})_5\cdot$ . This question was investigated using a modified version of the competition experiment designed by Fox *et. al.* [8]. For the reaction system  $\text{Mn}(\text{CO})_5\cdot + \text{L} + \text{RX}$  the applicable kinetic relationships are given either by equation (4),

$$\frac{[\text{Mn}(\text{CO})_4\text{LX}]}{[\text{Mn}(\text{CO})_5\text{X}]} = \frac{k_d}{ak_t} \frac{1}{[\text{L}]} + \frac{k_a}{ak_t} \quad (4)$$

where  $[\text{L}] = a[\text{RX}]$  and all other symbols are as defined by Fox *et. al.*, or by equation (5),

$$\frac{[\text{Mn}(\text{CO})_4\text{LX}]}{[\text{Mn}(\text{CO})_5\text{X}]} = \frac{k_d + k_a[1]}{k_t[\text{RX}]} \quad (5)$$

where the ratio  $[\text{L}]:[\text{RX}]$  is not fixed.

The experimental results show that for  $\text{L} = \text{PPh}_3$  and  $\text{RX} = \text{CCl}_4$ ,  $k_a = (1.8 \pm 0.2) \times 10^7 \text{M}^{-1}\text{s}^{-1}$  while  $k_d \leq 2.1 \times 10^3 \text{s}^{-1}$ , clearly demonstrating the reaction to be associative in character. The value of  $k_t$  was established to be  $(1.4 \pm 0.1) \times 10^6 \text{M}^{-1}\text{s}^{-1}$  by independent methods. A second system with  $\text{L} = \text{AsPh}_3$  and  $\text{RX} = \text{CH}_2\text{Br}_2$  lowered the limiting value of  $k_d$ :  $k_d \leq 9.0 \times 10^1 \text{s}^{-1}$ . Experiments with other phosphorus-based ligands demonstrated that both the steric and electronic properties of the incoming ligand are important in determining the rate constant of the reaction. The observed products for substitution of  $\text{Mn}_2(\text{CO})_{10}$  by L,  $\text{Mn}_2(\text{CO})_8\text{L}_2$  and  $\text{Mn}_2(\text{CO})_9\text{L}$  [6] are therefore proposed to result from substitution of  $\text{Mn}(\text{CO})_5\cdot$  and  $\text{Mn}_2(\text{CO})_9$ , respectively.





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